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TRANSFORMATIONS OF PARASULPHAMINEBENZOIC ACID UNDER THE INFLUENCE OF HEAT.

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In a recent article[1] it was stated that "when parasulphaminebenzoic acid is heated alone to a temperature near its melting-point it is completely transformed into other substances." The object of the investigation, the results of which are here presented, was to study these transformations carefully and to determine as far as possible their nature. As will be seen, the reactions which take place are of an unusual character, and they suggest further study in other groups. The point of chief interest is that, under the influence of heat, the nitrogen of the parasulphaminebenzoic acid passes from the sulphur atom, or, at least, from the sulphamine group to the carbon atom in the carboxyl. It appears highly probable that at 285° the principal reaction is that indicated below:

$$C_6H_4\begin{<}{CO.OH \atop SO_2NH_2} \rightarrow C_6H_4\begin{<}{CO.NH_2 \atop SO_2OH.}$$

At lower temperatures, however, products are obtained that are not easily soluble in water, and among them, an acid isomeric with parasulphaminebenzoic acid, and a compound isomeric with the diamide of parasulphobenzoic acid,

(1) [1] This JOURNAL, 18, 151.

$C_6H_4<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}$. The properties of these substances have been carefully studied, but, up to the present, no plausible hypothesis as regards their constitution has suggested itself. It is hoped, however, that further investigation may lead to a solution of the problem.

Method of Heating.

A cylindrical air-bath is surrounded with asbestos, so that by the use of one Bunsen burner the temperature within can be raised to 300°. The bath is covered with a glass plate, in the center of which is a hole for the insertion of a cork holding a thermometer. The temperature is regulated by means of a screw-clamp on the tubing of the burner. The parasulphaminebenzoic acid to be heated is ground very fine and placed in a small evaporating dish. The dish is covered with a watch glass, in the center of which is a small hole for the insertion of a thermometer. The bath is first heated to the desired temperature, and the flame regulated so that the temperature remains constant; then the dish is lowered to the shelf in the bath. The temperature of fusion can thus be accurately observed, as well as changes in color.

Changes at 285°.

If parasulphaminebenzoic acid is kept at 285° for three hours the resulting mass is somewhat colored, and is completely and easily soluble in water and in alcohol, but insoluble in benzene, ether, and ligroin. The opaque water solution was treated with bone-black, filtered and evaporated to crystallization, when, on cooling, crystals filled the liquid. These had the appearance of acid ammonium parasulphobenzoate, and were easily identified as such by comparing them with some of the salt made from parasulphaminebenzoic acid by treating it with hydrochloric acid in a sealed tube to 200°. On treating the solution of the salt with barium chloride, the acid barium salt of parasulphobenzoic acid was formed, and easily identified by the aid of its characteristic properties, and by its analysis:

0.3845 gram barium salt lost 0.035 gram H_2O, and gave 0.1493 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COOH}_{SO_3O})_2Ba.3H_2O$.	Found.
H_2O	9.11	9.10
Ba	23.10	22.83

The mother-liquor from the acid ammonium salt was evaporated after the addition of barium chloride, and on cooling, seed-like crystals were deposited in very small quantity. It is evident from the above that at 285° parasulphaminebenzoic acid is practically completely transformed into a substance which, when dissolved in water, is in turn transformed into acid ammonium parasulphobenzoate. The first change takes place without loss in weight, as was shown by a series of experiments, the results of which are recorded in the table below:

No.	Weight in grams of acid heated.	Weight in grams of acid after heating.	Temperature of heating.	Time of heating in hours.
I.	10.992	10.9655	220°	8
II.	4.56	4.525	225°	6
III.	4.8395	4.8475	235°	3
IV.	4.0235	4.026	235°	4
V.	3.9339	3.922	285°	3
VI.	5.001	5.886	285°	8

The facts observed show conclusively that the acid ammonium salt obtained cannot be formed in the first stage of the reaction, but that it must be formed when the first product is treated with water. In order to pass from parasulphaminebenzoic acid to acid ammonium parasulphobenzoate the addition of a molecule of water is obviously necessary:

$$C_6H_4<^{COOH}_{SO_2NH_2} + H_2O = C_6H_4<^{COOH}_{SO_3ONH_4}.$$

Now, this water is not formed at the expense of a part of the acid, and in consequence of a deep-seated reaction, for practically the only product formed is the one yielding the acid ammonium salt. Further, considering (1) that there is no loss in weight caused by the heating; (2) that the product is very easily soluble in water; and (3) that, as has been shown in a previous communication,[1] the nitrogen of the sulphamide group easily passes to the carbon of the carboxyl, it appears

[1] This JOURNAL, 18, 150.

not improbable that the first effect of heating parasulphaminebenzoic acid to 285° is to cause the amido group and the hydroxyl groups to exchange places:

$$C_6H_4<\begin{matrix}CO.OH\\SO_2.NH_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}CO.NH_2\\SO_2OH\end{matrix}.$$

According to this view, the first product is benzaminesulphonic acid. This being a sulphonic acid would probably be easily soluble in water and in alcohol. On the other hand, we have no means of judging whether a substance of this composition would take up water readily and yield the acid ammonium salt of parasulphobenzoic acid, but such a reaction would be quite analogous to others which are well known. The change in the position of the nitrogen atom suggested above is in some respects similar to that which takes place in the well known transformation of ammonium cyanate to urea, and in the reaction studied by Beckmann, and commonly called Beckmann's transformation. In the former case there is a shifting of the nitrogen atom from oxygen to carbon or from nitrogen to carbon:

$$N\equiv C-O-NH_4 \rightarrow O=C<\begin{matrix}NH_2\\NH_2\end{matrix},$$

or,

$$O=C=N-NH_4 \rightarrow O=C<\begin{matrix}NH_2\\NH_2\end{matrix};$$

and there is shifting of nitrogen from oxygen to carbon in Beckmann's reaction, as illustrated in the change of benzildioxim to oxanilide:

$$\begin{matrix}C_6H_5-C-C-C_6H_5\\ \quad\|\quad\ \|\\ HO-N\quad N-OH\end{matrix} \rightarrow \begin{matrix}O=C-C=O\\ \quad|\quad\ |\\ C_6H_5>N\quad N<C_6H_5\end{matrix}.$$

The transformation of diazoamidobenzene to amidoazobenzene, and that of hydrazobenzene to benzidine are also illustrations of this same tendency:

$$C_6H_5-N=N-NH.C_6H_5 \rightarrow C_6H_5-N=N-C_6H_4.NH_2;$$

$$C_6H_5-NH-NH-C_6H_4 \rightarrow \begin{matrix}C_6H_4.NH_2\\ |\\ C_6H_4.NH_2\end{matrix}.$$

Experiments are now in progress in this laboratory on the

action of heat on metasulphaminebenzoic acid, and these have already made it appear highly probable that the first change effected consists in an exchange of the amido group for hydroxyl, as suggested above. It is proposed, further, to study other cases as, for example, the sulphanilido acids of the formula $C_6H_4<\begin{matrix}COOH\\SO_2NHC_6H_5\end{matrix}$, and similar substances. It may in some cases be possible to isolate the intermediate products, and thus secure more satisfactory evidence in regard to the shifting of the nitrogen atoms.

Changes at 220° to 235°.

The lowest temperature at which a change takes place in parasulphaminebenzoic acid is 220°. If the temperature is kept between this point and 235°, a product insoluble in water, and quite different from parasulphaminebenzoic acid was obtained in varying quantities, according to the temperature. As shown in the table below, the lower the temperature the larger the yield of the insoluble product :

No.	Weight in grams of substance heated.	Grams of insoluble material formed.	Per cent. formed of insoluble material.	Temperature of heating.	Length of heating in hours.
I.	10.962	2.512	22.91	220°	8
II.	5.557	1.1338	20.4	223°	8
III.	4.56	0.8645	18.95	225°	6
IV.	6.132	1.1609	18.93	225°	6
V.	4.023	0.4825	11.98	235°	4

None of the original acid remained in any of these experiments.

Preparation of the Insoluble Product.—For the purpose of preparation the following method was found to be most satisfactory : Heat parasulphaminebenzoic acid at 220° for eight hours ; after cooling, powder the mass thus obtained. Treat with water, boil, and set the liquid aside over night, then filter, and wash with cold water. Dissolve the substance in cold caustic soda, treat with bone-black in the cold, and after the solution has stood for a short time with occasional stirring, filter with the aid of a pump. Treat the filtrate at once with a slight excess of hydrochloric acid, when the pro-

duct is deposited in characteristic crystalline form. Filter and wash free from hydrochloric acid.

When first formed the substance is in very finely divided condition, and, if filtration is attempted at once after treating the powdered mass with water, some of the undissolved product will pass through the filter. If, however, the mass is boiled with water, and allowed to stand for twelve hours, filtration is easy, and nothing is deposited from the filtrate on cooling.

The compound thus obtained is neutral toward litmus, is not dissolved by alkaline carbonates, is slightly soluble in boiling water, insoluble in cold and hot alcohol, and is infusible. It gives off ammonia copiously when boiled with a caustic alkali, and slowly even at low temperatures. It was analyzed with the following results:

I. 0.2118 gram gave 0.3264 gram CO_2, and 0.09 gram H_2O.

II. 0.1855 gram gave 0.286 gram CO_2, and 0.0709 gram H_2O.

III. 0.2455 gram gave 29.8 cc. of nitrogen at 18.4° and 762 mm.

IV. 0.2102 gram gave 25.96 cc. of nitrogen at 19.8° and 762 mm.

V. 0.1761 gram gave 0.2028 gram $BaSO_4$ (Carius method).

	Calculated for $C_7H_8SN_2O_3$.	Found.				
		I.	II.	III.	IV.	V.
C	42	42.02	42.04	....	....	....
H	4	4.51	4.25	....	....	....
N	14	....	....	14	14.14	....
S	16	....	....	....	....	15.9

The substance has, therefore, the same composition as the diamide of parasulphobenzoic acid, $C_6H_4<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}$, and it was at first supposed to be this, but further investigation showed conclusively that the two substances are not identical, and in the absence of clear evidence as to the relation between the two, the product obtained by heating parasulphaminebenzoic acid is here called the *infusible diamide*. This infusible diamide can be crystallized from water, but it is so difficultly

soluble, even in boiling water, that this does not commend itself as a method of purification. It does not dissolve in benzene, ligroïn, chloroform, or ether. Sodium hydroxide, as already stated, decomposes it even at low temperature, but neither boiling hydrochloric nor boiling nitric acid changes it. It dissolves readily even in cold concentrated sulphuric acid, and this solution can be heated to 200° without decomposition. On cooling and pouring into water, the characteristic crystals again appear. The crystals consist of small plates. If an excess of acid is added to a dilute alkaline solution, the minute plates appear slowly, and occasionally arrange themselves in rows forming needle-shaped crystals, which when disturbed break up into plates again. Even phosphorus pentachloride does not affect it easily; for, when heated with this reagent at 200° for several hours, the diamide was recovered unchanged.

Action of Concentrated Hydrochloric Acid on the Infusible Diamide at 200°.—The heating was continued for six hours. After the acid was evaporated, most of the residue dissolved easily in water, though there was a very small quantity of an insoluble substance left—too small for investigation. The soluble substance proved to be a mixture of acid ammonium parasulphobenzoate and ammonium chloride. The former was identified by its crystalline form and solubility, and the ease with which it yielded acid barium parasulphobenzoate. The barium salt was analyzed with the results below recorded:

0.2455 gram lost 0.0221 gram H_2O at 200°, and gave 0.0957 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COOH}_{SO_2O})_2Ba.3H_2O$.	Found.
H_2O	9.11	9.00
Ba	23.10	22.92

The reaction with hydrochloric acid is represented by the following equation:

$$p\text{-}C_6H_4<^{CONH_2}_{SO_2NH_2} + HCl + 2H_2O = C_6H_4<^{COOH}_{SO_2ONH_4} + NH_4Cl.$$

Action of Sodium Hydroxide on the Infusible Diamide.—In order to determine what proportion of the nitrogen is given

off as ammonia when the infusible diamide is treated with sodium hydroxide, the following experiment was made: 1.005 grams of the substance were placed in a small flask, about 20 cc. dilute sodium hydroxide added, and the ammonia distilled into an excess of dilute sulphuric acid of known strength. Titration showed that the weight of the ammonia given off was 16.9 per cent. of the weight of the substance taken, while, if all the nitrogen should be given off in this reaction, the weight of the ammonia would be 17 per cent. of that of the original substance. The solution left in the flask was neutralized, evaporated to dryness, and extracted with methyl alcohol. It was thus shown to contain the neutral sodium salt of parasulphobenzoic acid, which was converted in turn into the neutral barium salt and the acid barium salt, both of which were analyzed. The neutral salt gave these results:

0.7798 gram lost 0.0751 gram H_2O at 150°, and gave 0.484 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COO}_{SO_2O}>Ba.2H_2O$.	Found.
H_2O	9.65	9.63
Ba	36.73	36.50

The acid salt gave these results:

0.5113 grhm lost 0.0466 gram H_2O at 200°, and gave 0.2001 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COOH}_{SO_2O})_2Ba.3H_2O$.	Found.
H_2O	9.11	9.11
Ba	23.10	23.01

Sodium hydroxide, therefore, easily drives out all the nitrogen from the infusible diamide, the reaction being represented by the equation:

$$C_6H_4<^{CONH_2}_{SO_2NH_2} + 2NaOH = C_6H_4<^{COONa}_{SO_2ONa} + 2NH_3.$$

Experiments were next made with the object of determining whether half the nitrogen could be eliminated, and an intermediate product formed, but without success. If decomposition takes place at all, it is complete as far as it goes. A

portion of the infusible diamide was allowed to stand for two months in strong hydrochloric acid, and another portion dissolved in concentrated sulphuric acid was allowed to stand for the same time, but no change was observed in either case. A weighed quantity was then boiled with a solution containing only half enough potassium hydroxide to drive off all the nitrogen, but it was found that part of the diamide was converted into neutral potassium parasulphobenzoate, while the rest remained unchanged. It was also found to be impossible to obtain an intermediate product by letting the infusible diamide stand in sodium hydroxide solution. Even at temperatures below 0° only a short time was required to drive out all the nitrogen.

Preparation and Properties of the Fusible or Normal Diamide of Parasulphobenzoic Acid.

The properties of the infusible diamide described in the preceding section make it difficult to believe that it is the normal diamide of parasulphobenzoic acid. Substances containing the sulphamide group, SO_2NH_2, do not easily give up the nitrogen of this group in the form of ammonia, nor, indeed, is the group $CO.NH_2$, as it usually presents itself, easily decomposed by acid or by alkali. Attempts were accordingly made to prepare the normal diamide by means of the ordinary reactions. First, parasulphaminebenzoic acid was converted into the acid ammonium salt of parasulphobenzoic acid by heating with hydrochloric acid to 200° in a sealed tube. From the acid ammonium salt, the neutral potassium salt was made, and this converted into the dichloride by phosphorus pentachloride. The dichloride can be crystallized from benzene in stout, transparent plates. By treating it with ammonia it is converted into the diamide. This proved, however, to be quite different from the infusible diamide. After crystallization from water it was found to have the properties of a pure substance, and it was analyzed with the results given below:

I. 0.2064 gram gave 0.0815 gram H_2O and 0.318 gram CO_2.

II. 0.3327 gram gave 0.1226 gram H_2O and 0.5132 gram CO_2.

III. 0.1846 gram gave 22.4 cc. of nitrogen at 20° and 773.1 mm.

IV. 0.1361 gram gave 16.75 cc. of nitrogen at 20° and 763.65 mm.

V. 0.1701 gram gave 0.1982 gram $BaSO_4$ (Carius).

	Calculated for $C_6H_4<^{CO.NH_2}_{SO_2NH_2}$	Found.				
		I.	II.	III.	IV.	V.
C	42	42.01	42.09	....	....	....
H	4	4.39	4.20	....	....	....
N	14	....	....	14.10	14.12	....
S	16	....	....	....	....	16.01

As was to be expected from the method of formation, the substance is the diamide. That it is entirely different from the infusible diamide will appear from the account of its properties. Like the infusible substance, it is neutral and insoluble in alkaline carbonates, and it gives off ammonia when boiled with the caustic alkalies. But, while the infusible diamide is extremely difficultly soluble in boiling water, the new compound dissolves readily in boiling water, and is deposited in needles from the solution on cooling. Again, the infusible compound is insoluble in alcohol, while the fusible isomer is soluble. It melts sharply at 230°. Both substances dissolve in caustic soda. From this solution the infusible diamide is precipitated by acids in minute, lustrous plates, the fusible in milky form.

Action of Acids on the Fusible Diamide.—When heated at 200° in a sealed tube for six hours, with hydrochloric acid, the fusible diamide is completely transformed into acid ammonium parasulphobenzoate and ammonium chloride, just as the infusible compound is. The ammonium salt was transformed into the acid barium salt, and this was analyzed.

0.5298 gram lost 0.0483 gram H_2O at 200°, and gave 0.2073 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COOH}_{SO_2O})_2Ba.3H_2O$.	Found.
H_2O	9.11	9.11
Ba	23.10	23.00

Only ammonium chloride was found in the mother-liquor from the acid ammonium salt.

Action of Sodium Hydroxide on the Fusible Diamide.—When

the fusible diamide is boiled with sodium hydroxide, ammonia is readily given off. If the boiling is continued as long as ammonia is evolved, the solution obtained gives a copious precipitate with hydrochloric acid. This proved to be easily soluble in sodium carbonate, insoluble in cold water, and difficultly soluble in hot water, from which it crystallized in needles melting at about 280°. This is parasulphaminebenzoic acid, as is clearly shown by the facts stated, and, further, by the properties and analysis of the barium salt. This crystallized in spherical clusters, as described by Remsen[1] and by Noyes.[2] It was analyzed with the results given below:

0.2145 gram of salt lost 0.0313 gram H_2O at 160°, and gave 0.0789 gram $BaSO_4$.

	Calculated for $(C_6H_4<^{COO}_{SO_2NH_2})_2Ba.5H_2O$.	Found.
H_2O	14.35	14.59
Ba	21.85	21.64

Even in the cold, sodium hydroxide affects this decomposition, though much more slowly than in the case of the infusible diamide. At 18° two weeks were required, but at 0° two months were necessary. The precipitate obtained in these cases on acidifying proved to be parasulphaminebenzoic acid.

While, therefore, the infusible diamide readily gives up all of its nitrogen as ammonia when treated with an alkali, the fusible diamide gives up only half of its nitrogen, the other half remaining in combination in the form of the stable sulphamide group, SO_2NH_2. In other words, the fusible diamide conducts itself as we should expect it to, if it has the constitution represented by the formula $C_6H_4<^{CONH_2}_{SO_2NH_2}$, while the infusible diamide of the same composition does not so conduct itself.

Special experiments showed that when the fusible diamide is boiled with sodium hydroxide, the sulphamide group is not at all affected, no parasulphobenzoic acid being formed.

Preparation of the Fusible Diamide from Parasulphaminebenzoic Acid.—Parasulphaminebenzoic acid was converted into the chloride by treating the potassium salt with phosphorus

[1] Ann. Chem. (Liebig), **178**, 302. [2] This JOURNAL, **7**, 147.

pentachloride, extracting with anhydrous ether, and passing dry ammonia into the ethereal solution. In this way a compound was obtained having the properties of the diamide described in the preceding section. It crystallized in the same way and melted at 230°. It gave off ammonia when boiled with caustic soda, and the solution thus formed gave a precipitate of parasulphaminebenzoic acid when acidified. It was only after many experiments that the above method was devised. At first, the product formed with phosphorus pentachloride was treated with water, and the insoluble material, after filtering and washing, was treated with aqueous ammonia. On acidifying this solution, only parasulphaminebenzoic acid was obtained.

Preparation of the Fusible Diamide from Ethyl Parasulphaminebenzoate.—The ethyl salt of parasulphaminebenzoic acid was prepared by treating the chloride of the acid with alcohol and by the usual method. In order to convert it into the corresponding amide, it was treated with aqueous ammonia. It dissolved at once, and, on acidifying, only parasulphaminebenzoic was precipitated. Next, some of the ethereal salt was dissolved in absolute alcohol, the solution saturated with dry ammonia, and the whole heated in a sealed tube at 100° for a day, but the ethereal salt was recovered unchanged. Finally some of the dry ethereal salt was kept at 100° in a flask, and dry ammonia passed over it, but no change took place until the temperature was raised to 170°, when decomposition set in. The mass was charred but, nevertheless, it was extracted with hot water. In this way some of the ethereal salt was recovered unchanged, and a little of the amide was also obtained. The difficulty with which this change of the ethereal salt to the amide takes place is remarkable.

Comparison of the two Diamides.

The work above described shows conclusively that two substances of the composition of the diamide, $C_6H_4<\begin{matrix}CONH_2\\SO_2NH_2\end{matrix}$, can be obtained from parasulphobenzoic acid. By starting with this acid we have passed through the chloride to the diamide. This loses one of its nitrogen atoms easily and gives parasulph-

aminebenzoic acid; and the latter can be reconverted into the diamide by means of the usual reactions. There is no reason for supposing that the diamide thus formed is anything but the normal compound, containing the ordinary carbamide group and the ordinary sulphamide group. But what is the isomeric compound, the so-called infusible diamide? There is no room for doubt in regard to its composition. It is unquestionably isomeric with the fusible or normal diamide. It may contain the group $CONH_2$, identical with that contained in the normal diamide; though this does not appear probable in view of the ease with which it gives up all of its nitrogen; but it cannot contain the ordinary sulphamide group, SO_2NH_2, which, as is well known, is extremely stable. The compound is a derivative of parasulphobenzoic acid, as appears from the ease with which it can be converted into salts of this acid. The facts thus far established plainly do not suffice to enable us to draw a conclusion in regard to the relation between the two diamides. Stereochemistry appears to be of no avail in this case, and, while it is possible to write different structural formulas for compounds of this composition, that would not be a profitable occupation without further data. One would be inclined to suspect some rearrangement of the constituents of each of the two groups, $CO.NH_2$ and $SO_2.NH_2$. These might become respectively $-C\begin{matrix}OH\\ \diagup\\ \diagdown\\ NH\end{matrix}$ and $O=\begin{matrix}|\\ S-OH\\ ||\\ NH\end{matrix}$; but, as it will be extremely difficult to test these ideas by experiment, they are worth practically nothing.

It has not been found possible to change one diamide into the other. The fusible substance was heated for some time just above its melting-point, but no trace of the isomer could be found in the product. Some of the infusible substance was heated with water alone in a sealed tube, but no change was effected through comparatively wide ranges of temperature.

Isoparasulphaminebenzoic Acid.

The filtrates from the infusible diamide (see p. 353), ob-

tained by heating parasulphaminebenzoic acid at 220–235°, were collected, purified by means of bone-black, and evaporated to crystallization. Six successive deposits were obtained. The first three were alike. The other three were small in quantity, appearing to consist chiefly of an acid that formed an insoluble barium salt crystallizing in fine, voluminous needles. The final mother-liquor was evaporated to dryness, and found to contain very little nitrogen. Three different substances were thus obtained. The first was found to be acid ammonium parasulphobenzoate. After many experiments, it is safe to say that, when parasulphaminebenzoic acid is heated at 220–235°, about 25 per cent. of it is changed in the same way that nearly all of it is changed at 285°, so that, on treating it with water, it yields acid ammonium parasulphobenzoate.

The final residue referred to above as containing very little nitrogen proved to be free parasulphobenzoic acid, which was identified by means of the characteristic acid barium salt. The quantitiy of this acid formed differed in different experiments. Its formation may be accounted for by supposing that it runs parallel with the formation of the diamide as indicated in the equation :

$$2C_6H_4{<}\begin{matrix}COOH\\SO_2NH_2\end{matrix} = C_6H_4{<}\begin{matrix}CONH_2\\SO_2NH_2\end{matrix} + C_6H_4{<}\begin{matrix}COOH\\SO_2OH\end{matrix}.$$

The intermediate product above mentioned as yielding a barium salt that crystallizes in fine, voluminous needles proved to be a compound of special interest. It is this to which the name *isoparasulphaminebenzoic acid* is given for reasons that will appear. In order to prepare the substance, it is best to proceed thus : After heating parasulphaminebenzoic acid at 220° for eight hours, pulverize the product and extract with hot alcohol. A flocculent substance will then be deposited from the filtrate on cooling. When its solution in water is treated with barium chloride, the characteristic needles of the barium salt are formed. The salt was recrystallized from hot water and analyzed with the following results :

I. 0.2182 gram salt lost 0.0137 gram H_2O at 150°, 0.0202 gram H_2O at 200°, and gave 0.086 gram $BaSO_4$.

II. 0.1916 gram salt gave 8.2 cc. of nitrogen at 18° and 749.45 mm.

III. 0.1342 gram salt gave 0.103 gram $BaSO_4$ (Carius).

	Calculated for $(C_6H_4<^{COO}_{SO_2NH_2})_2Ba.3H_2O$.	Found. I.	II.	III.
$2H_2O$	6.09	6.28	....	....
$3H_2O$	9.14	9.21	....	....
Ba	23.18	23.17	....	....
N	4.73	....	4.86	....
S	10.82	....	....	10.54

It will be seen that the salt is derived from an acid isomeric with parasulphaminebenzoic acid. When dissolved in water, it crystallizes out on cooling in exceedingly fine needles so intricately interwoven that, when the salt is deposited from a saturated solution, the vessel containing it can be inverted without loss of material, though the saturated solution contains only 1 per cent. of the salt.

Free isoparasulphaminebenzoic acid is very soluble in water. Several of its salts were made, but only the ammonium and barium salts are at all well characterized. The former crystallizes in short, stout, transparent prisms, quite different from the glistening aggregates of needles formed by ammonium parasulphaminebenzoate. The calcium, strontium, zinc, magnesium, and lead salts of the two isomeric acids were made, and compared side by side. Those of parasulphaminebenzoic acid are well defined, the zinc salt being especially beautiful, while those of the iso acid are amorphous, and all except the lead and barium salts are very easily soluble. The analytical results obtained, except in the case of the barium salt, were quite variable and unsatisfactory. The mercury and silver salts were made also, but they are equally uninviting.

Action of Potassium Hydroxide on Isoparasulphaminebenzoic Acid.—The fact that the free acid is easily soluble in water, and isomeric with parasulphaminebenzoic acid led to the suspicion that it might be benzaminesulphonic acid $C_6H_4<^{CONH_2}_{SO_2OH}$ But experiment showed that this view is highly improbable. It has already been shown that the carbamine group readily

gives up its nitrogen as ammonia under the influence of alkalies. This acid, however, gives up its nitrogen with great difficulty. No ammonia was given off on boiling with a concentrated solution of potassium hydroxide, and it was not until the hydroxide was practically free from water, and the temperature high enough to drive out the sulphonic acid group that ammonia was detected. The product formed under these circumstances is parahydroxybenzoic acid, as was shown by the melting-point and other properties.

Effect of Heating Isoparasulphaminebenzoic Acid with Hydrochloric Acid at 270°.—The acid is not as easily changed by heating with hydrochloric acid as is parasulphaminebenzoic acid. A temperature of 270° seemed to be necessary to effect anything like a complete change. For the purpose of the experiment, the barium salt was used instead of the free acid. After precipitating the barium from the solution, a very small quantity of a substance appeared in flocculent form, but the quantity was so small as to render an investigation impossible. Almost all of the material left, after heating with hydrochloric acid and evaporating to dryness, is soluble in cold water. This proved to be nothing but the acid ammonium salt of parasulphobenzoic acid, the same product that is formed under similar circumstances, though at lower temperature, from parasulphaminebenzoic acid.

Attempt to Prepare the Amide of Isoparasulphaminebenzoic Acid.—In the thought that the amide of isoparasulphaminebenzoic acid might be identical with one or the other of the two diamides described in the early part of this article, an attempt was made to prepare it, but this was unsuccessful. The dried salt of the acid was thoroughly mixed with an equivalent quantity of phosphorus pentachloride, and the mass gently warmed. Reaction took place easily, and, on the addition of water, a white substance separated. This was found to contain chlorine and to be free from phosphorus. It was quite insoluble in every solvent tried. On boiling with an alkali, it passed into solution, and, on acidifying and cooling, no precipitate was formed; but, on rendering the solution slightly alkaline with ammonia, and adding barium chloride,

a precipitate was formed. On crytallizing this from water it proved to be the barium salt of isoparasulphaminebenzoic acid. When the chlorine derivative of the iso acid is treated with aqueous ammonia it dissolves at once; and when this solution is acidified a gelatinous mass is precipitated much like aluminic hydroxide.

Lack of material prevented further investigation of the isoparasulphamine acid and its derivatives; and we are entirely at a loss to form any conception in regard to the relations existing between it and the ordinary parasulphaminebenzoic acid. In this connection, it should be mentioned that, in their study of metasulphaminebenzoic acid, Limpricht and Uslar[1] isolated two acids isomeric with their sulphamine acid, one very soluble in water the other insoluble and amorphous. They succeeded in transforming the amorphous acid into the ordinary variety by heating it with water in a sealed tube to 170–180°. A similar experiment was made with free isoparasulphaminebenzoic acid, but apparently no change took place.

Further efforts will be made to discover the nature of the curious and, at present, inexplicable compounds described in this article.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
March, 1896.

THE HEAT OF ELECTROLYTIC DISSOCIATION OF SOME ACIDS.[2]

BY F. L. KORTRIGHT.

The heat of electrolytic dissociation of a number of acids has been determined by Arrhenius[3] and Jahn,[4] but in each case it has been with acids which do not obey the Ostwald dilution law or else belong to one particular class of organic acids. It has therefore seemed desirable that measurements should be made on a number of acids of different but allied constitution, and thus a study made of the effect of constitution upon the heat of electrolytic dissociation.

[1] Ann. Chem. (Liebig), **106**, 43.

[2] The measurements for the above were made at the suggestion of Professor Trevor during the summer of 1894, but were not published at that time in the hope that they might be further extended.

[3] Ztschr. phys. Chem., **4**, 96; **9**, 360. [4] Ztschr. phys. Chem., **16**, 72.

The conductivity measurements were made by means of the well-known Ostwald-Kohlrausch method described in Ostwald's Handbuch fur physiko-chemische Messungen, page 266, using the Arrhenius resistance cell (Fig. 176 of the above book).

A wooden pail having an inside diameter of 6 inches, a depth of 10 inches, and walls an inch thick, was employed as a thermostat. It was kept immersed in a larger pail of ice water. The inner pail was filled with a slush of clean finely pulverized ice, which gave a very constant temperature of 0°. A thermometer divided into tenths of a degree placed near the resistance cell never showed over 0.03° variation from 0° at the time of taking the bridge reading.

The water employed was taken from a spring, carefully distilled through block tin condensers from alkaline permanganate into phosphoric acid, and then into a carboy. The carboy had previously contained ammonium hydroxide, but before using it was carefully washed out with hydrochloric acid and then with running water for several days. The water thus prepared gave a specific conductivity at 0° of 1.7×10^{-6}.

The conductivities of the salt solutions were corrected by subtracting the molecular conductivity of the water from that of the salt solution; with the acids no correction was applied.

The potassium salts of the various acids were prepared by running a standard solution of potassium hydroxide (made from metallic potassium and carefully kept from carbon dioxide) upon the solid acid until the color of phenolphthalein appeared, and then adding a small amount of solid acid to cause the color to disappear, thus guarding against the presence of any excess of potassium hydroxide. This salt was then diluted to a concentration of one mol in 32 liters of water.

The concentration of the acid solution was determined in each case by titrating with a standard solution of barium hydroxide, using phenolphthalein as an indicator. The barium hydroxide solution was standardized by titrating against carefully purified, dried, and weighed portions of succinic acid.

In order to obtain μ_∞ for the acids by use of the formula $\mu_{\infty\ \text{acid}} = \mu_{\infty\ \text{HCl}} - \mu_{\infty\ \text{KCl}} + \mu_{\infty\ \text{KR}}$, which seems to be the most nearly correct of anything we have at present, it is necessary to know the conductivity at infinite dilution and at 0° of hydrochloric acid, potassium chloride, and the potassium salt of the acid in question. The μ_∞ for potassium chloride at 0° was obtained from the extrapolation formula of Déguisne,[1]

$$\mu_t = \mu_{18}[1 + \alpha\,(t - 18) + \beta\,(t - 18)^2]$$

where $\mu_{\infty\ 18^\circ} = 123$,[2] and for 1 mol in about 20,000 liters of water $\alpha = 2194 \times 10^{-5}$, and $\beta = 324 \times 10^{-7}$. This gave 77.7, while direct measurements by R. W. Wood[3] gave 77.8. μ_∞ for hydrochloric acid at 0° obtained from Déguisne's formula where $\mu_{\infty\ 18^\circ} = 353$, and for 1 mol in 10,000 liters of water $\alpha = 1660 \times 10^{-5}$ and $\beta = 92 + 10^{-7}$, is 248.5. Kohlrausch[4] gives 208 as the migration velocity of hydrogen at 0° and, since the transference number of chlorine in potassium chloride is nearly independent of the temperature, *i. e.*, 0.510 according to Hittorf, $77.7 \times 0.510 = 39.6$ is the migration velocity of chlorine. Therefore, $208 + 39.6 = 247.6$ is the μ_∞ of hydrochloric acid at 0° according to Kohlrausch. The mean of these two values is about 248, which is adopted as the μ_∞ for hydrochloric acid at 0°. The μ_∞ at 0° of the potassium salts of the acids was obtained by determining the conductivity of the salts prepared as above at dilutions of 1 mol salt in 32, 64, 128, 256, 512, and 1024 liters of water, and adding to these values of μ_v the proper increment as given from $\mu_\infty - \mu_v = n_1 n_2 C$. Where n_1 and n_2 are the valences of the ions, and C is a constant for constant volume and temperature. The various values for C were taken from Wood's[5] table for the conductivity of potassium chloride at 0°, and checked against the values of C at 25° given by Breidig.[6] The μ_∞ for the potassium salt calculated from the μ_v of the salt at different concentrations was very nearly constant and a suitable average of these values gives a very

[1] Temperatur-Coëfficienten des Leitvermögens sehr verdünnter wässriger Lösungen. Inaug. Dissert., p. 14.

[2] Kohlrausch, Ann. Phys. (Wiedeman), **50**, 406, 1893.

[3] Ztschr. phys. Chem., **18**, 322.

[4] Ztschr. phys. Chem., **14**, 326.

[5] *Loc. cit.*

[6] Ztschr. phys. Chem., **13**, 198.

nearly correct value for the μ_∞ of the various potassium salts. Therefore, by taking

$$\mu_{\infty\,\text{acid}} = 248 - 77.7 + \mu_{\infty\,\text{KR}},$$

we obtain the μ_∞ for the various acids, and from the measurements of their conductivities their affinity constants may be calculated.

Very pure acids were employed for the measurements; the butyric, malonic, maleïc, fumaric, mesaconic, citraconic, ortho- and metaphthalic acids were kindly furnished me by Professor Trevor and were from the preparations used by him in his work on the measurement of small degrees of dissociation.[1] The monobromacetic acid was obtained specially pure from Kahlbaum. The benzoic, succinic, and monochloracetic acids were several times recrystallized.

In the following tables, under v is the number of liters solution containing 1 mol. of acid; μ_∞ is, as usual, the conductivity at infinite dilution; μ_v the conductivity at a dilution v; 100α the percentage of electrolytic dissociation of the acid; $100k$ the affinity constant calculated according to the Ostwald dilution law; Kt.K is the most probable affinity constant of the acid at 0° from my measurements; Ost.K is the most probable affinity constant at 25° as given by Ostwald.

Monochloracetic Acid.—$\mu_\infty = 229$.

v.	μ_∞.	100α.	$100k$.
32	48.88	21.34	0.181
64	65.21	28.47	0.177
128	85.21	37.21	0.172
256	109.4	47.77	0.170
512	135.9	59.34	0.169
1024	162.6	71.00	0.170

Kt.K = 0.181 Ost.K = 0.155

Monobromacetic Acid.—$\mu_\infty = 229$.

32	45.79	19.99	0.156
64	61.13	26.69	0.152
128	80.66	35.22	0.150
256	103.91	45.37	0.147
512	130.24	56.87	0.146

Kt.K = 0.156 Ost.K = 0.138

[1] Ztschr. phys. Chem., **10**, 321.

Malonic Acid.—$\mu_\infty = 240$.

16	32.93	13.72	0.136
32	44.69	18.61	0.133
64	59.83	24.93	0.129
128	78.92	32.90	0.126
256	102.14	42.56	0.123

Kt.K = 0.136 Ost.K = 0.158

Butyric Acid.—$\mu_\infty = 225$.

16	3.64	1.618	0.00166
32	5.17	2.298	0.00169
64	7.34	3.262	0.00171
128	10.34	4.595	0.00172
256	14.48	6.435	0.00172

Kt.K = 0.00166 Ost.K = 0.00149

Benzoic Acid.—$\mu_\infty = 225$.

64	13.76	6.12	0.00623
128	19.34	8.60	0.00632
256	26.93	11.97	0.00631
512	37.05	16.47	0.00634
1024	50.85	22.60	0.00644

Kt.K = 0.00632 Ost.K = 0.00600

Orthophthalic Acid.—$\mu_\infty = 236$.

64	56.51	23.94	0.118
128	74.77	31.68	0.115
256	97.00	41.10	0.112
512	122.20	51.78	0.109
1024	149.04	63.15	0.105

Kt.K = 0.118 Ost.K = 0.121

Metaphthalic Acid.—$\mu_\infty = 236$.

626	70.31	29.79	0.0202
1252	94.04	39.85	0.0211
2504	124.70	52.83	0.0236

Kt.K = 0.0202 Ost.K = 0.0287

Succinic Acid.—$\mu_\infty = 238$.

32	9.547	4.01	0.00523
64	13.24	5.56	0.00511
128	18.51	7.77	0.00511
256	25.69	10.79	0.00510
512	35.62	14.95	0.00513
1024	49.25	20.69	0.00527

Kt.K = 0.00511 Ost.K = 0.00665

Maleïc Acid.—$\mu_\infty = 239$.

32	107.49	44.97	1.14
64	132.31	55.36	1.07
128	156.44	65.45	0.97
256	179.71	75.19	0.89
512	198.55	83.07	0.80
1024	212.30	88.82	0.69
	Kt.K = 1.14	Ost.K = 1.30	

Fumaric Acid.—$\mu_\infty = 240$.

32	35.48	14.78	0.0801
64	48.42	20.17	0.0796
128	65.36	27.23	0.0796
256	86.75	36.14	0.0799
512	113.01	47.09	0.0818
1024	143.45	59.77	0.0867
	Kt.K = 0.0800	Ost.K = 0.093	

Mesaconic Acid.—$\mu_\infty = 237$.

64	45.95	19.38	0.0729
128	62.11	26.20	0.0727
256	82.23	34.70	0.0720
512	106.24	44.83	0.0711
1024	134.17	56.61	0.0721
	Kt.K = 0.0729	Ost.K = 0.0790	

Citraconic Acid.—$\mu_\infty = 235$.

64	89.85	38.23	0.369
128	113.84	48.44	0.355
256	139.55	59.38	0.339
512	164.42	69.96	0.318
1024	185.99	79.15	0.293
	Kt.K = 0.369	Ost.K 0.340	

Since the rate of change of the affinity constant with the temperature is given by the van't Hoff equation,

$$\frac{\partial \log K}{\partial T} = \frac{J q}{R T^2}$$

where K is the affinity constant, T the absolute temperature, q the heat of electrolytic dissociation, J the mechanical equivalent of heat, and R the gas constant, we may by integrating and solving for q obtain the value for the heat of electrolytic dissociation. Integrating the above equation between K_1 and K_2 under the assumption that q is independent of the

temperature which is not far from correct for small temperature differences, we get

$$\log K_2 - \log K_1 = \frac{J\,q}{R} \cdot \frac{T_2 - T_1}{T_1\,T_2}.$$

Solving for q and substituting the values for J, R and the factor for changing natural logarithms to the base 10, gives

$$q = \frac{4.56\ (\log_{10} K_2 - \log_{10} K_1)\ T_1\,T_2}{T_2 - T_1}$$

where positive q is heat absorbed if the process takes place without outside work.

The heats of electrolytic dissociation, calculated from the above formula by substituting the values of K_1 from the above tables, K_2 from Ostwald's measurements at 25° and the proper temperature values, appear in the following table:

Acid.	Formula.	q 12.5°.	
Acetic	CH_3COOH	−428	cal. J^1
Monochloracetic	$CH_2ClCOOH$	−999	"
Monobromacetic	$CH_2BrCOOH$	−790	"
Dichloracetic	$CHCl_2COOH$	−2924	" A
Malonic	$CH_2(COOH)_2$	+966	"
Butyric	C_3H_7COOH	−696	"
Benzoic	C_6H_5COOH	−335	"
Orthophthalic	$C_6H_4(COOH)_2$	+162	"
Metaphthalic	$C_6H_4(COOH)_2$	+2260	"
Succinic	$C_2H_4(COOH)_2$	+1697	"
Maleïc	$C_2H_2(COOH)_2$	+846	"
Fumaric	$C_2H_2(COOH)_2$	+970	"
Mesaconic	$C_3H_4(COOH)_2$	+518	"
Citraconic	$C_3H_4(COOH)_2$	−522	".

The above table confirms the result of Arrhenius and Jahn that the monobasic acids dissociate electrolytically with an evolution of heat; it also shows that the evolution of heat is increased by the introduction of a halogen, and that the effect of a second halogen is greater than that of the first. On the other hand, the introduction of a carboxyl group into the acid causes an absorption of heat, and the further the carboxyl groups are removed from each other the greater the absorption of heat.

[1] The value of q marked J is taken from Jahn's table at 18°, that marked A from Arrhenius table at 21.5°.

CORNELL UNIVERSITY, March, 1896.

Contribution from the Laboratory of General Chemistry, University of Michigan.

ON THE EXISTENCE OF PENTAETHYL NITROGEN.

By Arthur Lachman.

There is *a priori* no reason why nitrogen in its pentavalent state cannot combine with five *like* atoms or radicals, just as in its trivalent state it unites with three like atoms. And there is, further, no reason known why in pentavalent nitrogen compounds, the atoms or radicals attached to the nitrogen must consist of two groups, strongly contrasted (*e. g.*, $H_4\equiv N-Cl$, $(CH_3)_3\equiv N=ICl$, $C_6H_5-N\equiv O_2$). The existence of a compound NX_5, therefore, is not contradicted by anything but experience; and it seemed well worth the effort to attempt its preparation. The pentachloride, NCl_5, was not to be thought of; the hydrogen compound, NH_5, presented no point of attack; but for the pentaethyl compound, $N(C_2H_5)_5$, one method in particular suggested itself, which has been very frequently employed in the carbon series, and which had been successful in the one case where it was tried with (trivalent) nitrogen.

This method is the action of zinc alkyl on alkyl halogen substitution products of the hypothetical compound, NH_5. Tertiary butyl iodide,[1] $(CH_3)_3CI$, reacts immediately with zinc ethyl, and tetraethylammonium iodide, $(C_2H_5)_4NI$, seems to be structurally analogous. Triethylamine dibromide,[2] $(C_2H_5)_3NBr_2$, appears to present even a more favorable case, as Tscherniak[3] had successfully prepared triethylamine by the action of zinc ethyl on ethyldichloramine, $(C_2H_5)NCl_2$. The experiments were confined to these two substances.

Action of Zinc Ethyl on Tetraethylammonium Iodide.

Strange to say, tetraethylammonium iodide and zinc ethyl do apparently react. The action is very slow; heating on the water-bath for several hours produces no effect, nor does standing at ordinary temperature for ten days. But if, after standing from four to six weeks, a mixture of the substances in question (slightly diluted with ether to give fluidity to the mass) is poured into water and filtered from the

[1] Ann. Chem. (Liebig), **165**, 107.

[2] The kindness of Dr. J. F. Norris enabled me to use this compound instead of the more difficultly accessible $(CH_3)_3NICl$.

[3] Ber. d. chem. Ges., **9**, 143.

zinc hydrate,[1] the solution possesses a *strongly alkaline* reaction. It slowly turns yellow, and then a finely crystalline red precipitate separates. This precipitation is not hastened by carbon dioxide; in the experiment that was carefully controlled it required a day and a half for completion.

10 grams tetraethylammonium iodide, 5 grams zinc ethyl, and 15 cc. ether stood for 43 days at the ordinary working temperature, and yielded 0.61 gram of the red substance. This red substance, by properties and analysis, seems to be tetraethylammonium triiodide, $(C_2H_5)_4NI_3$. (Found 73.4 per cent. iodine, calculated 74.5 per cent.; the crude product was analyzed directly).

I am at a loss to explain this curious reaction. The formation of an alkaline[2] substance is in itself peculiar. The alkaline body could not be isolated nor in any way identified owing to the very small quantity formed; in evaporating the solution saturated with carbon dioxide, the alkaline reaction disappeared. The precipitation of tetraethylammonium triiodide from an *alkaline* solution, which could not have contained any free iodine, is quite inexplicable.

Action of Zinc Ethyl on Triethylamine Dibromide.[3]

This reaction presented three possibilities:

I. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_4N + ZnBr_2$.

II. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_4NBr + Zn(C_2H_5)Br$.

III. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_3N + C_2H_5Br + Zn(C_2H_5)Br$.

Reactions I and II would represent actual syntheses; reaction III would involve reduction. Experiment showed that reaction III took place, to the exclusion[4] of the others. It seems superfluous to give the details of work which has no preparative value; but every product of the action was iden-

[1] It was impossible to determine satisfactorily whether this zinc hydrate contained basic zinc iodide, and thus ascertain whether the zinc ethyl had reacted in the usual manner. The hydrate retained tetraethylammonium iodide so tenaciously that even after washing for several days with water and alcohol, the filtrate still gave a distinct reaction with silver nitrate.

[2] It is not impossible that this alkaline substance is really pentaethyl nitrogen, but alkalinity is hardly a property it would be expected to possess.

[3] This was prepared according to Remsen and Norris. This JOURNAL, 18, 90.

[4] A minor reaction, represented by the equation $(C_2H_5)_3NBr_2 + Zn(C_2H_4)Br = (C_2H_5)_3N + C_2H_4Br + ZnBr_2$, also took place.

tified. As a matter of fact, in some cases where the mixture of zinc ethyl and the dibromide (always diluted with considerable chloroform) was allowed to stand several hours, as much as 33 per cent. of the total nitrogen employed was obtained as tetraethylammonium bromide; but this was due to a secondary action,—the addition of ethyl bromide to triethylamine—for, if the mixture was examined shortly after its preparation, no quaternary ammonium compound could be found.

No synthesis whatever, then, had been accomplished. Triethylamine dibromide, in its action toward zinc ethyl, behaves merely as a mixture of triethylamine and bromine. It will be interesting to learn from Dr. Norris whether it behaves thus in every case. In this connection, it may be remarked that ethyl dichloramine, which reacts normally with zinc ethyl, acts like free chlorine in some instances.[1]

Perhaps pentaethyl nitrogen will be prepared by some one more fortunate, by means at present undiscernible. The experiments just sketched will not be continued.

Action of Zinc Ethyl on Phenyl Iodide Chloride.

This may be the place to briefly give an account of the action of zinc ethyl on phenyl iodide chloride, $C_6H_5I.Cl_2$, which possesses some analogy to triethylamine dibromide, and the study of which I took up for that reason. Both are halogen addition-products, a sort of half-way station between the more stable derivative of elements exhibiting two valencies. One might reasonably expect to obtain, in this case, a semi-aliphatic analogue, $\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix} > ICl$, of the very stable iodonium compounds of Hartmann and Victor Meyer. The reaction, however, is exactly analogous to that of the dibromide: phenyl iodide, ethyl chloride, zinc chloride, and zinc oxychloride are the final products. There are indications that an unstable intermediate addition-product is formed. It was possible to show analytically that almost exactly half of the total chlorine was regained as zinc chloride (and oxychloride); the other half could not be accurately traced: the phenyl

[1] Ber. d. chem. Ges., **16**, 1047.

iodide was recovered unaltered, and in practically theoretical quantity, but only a small percentage of ethyl chloride could be isolated.

ANN ARBOR, MICH.

THE CONDUCTIVITY OF SOLUTIONS OF ACETYLENE IN WATER.[1]

BY HARRY C. JONES AND CHARLES R. ALLEN.

Keiser[2] has shown by his work on the metallic compounds of acetylene, that both the hydrogen atoms possess acid properties, being capable of substitution by some metals. The compounds of silver and copper are formed by the substitution of two univalent metallic atoms for the two hydrogen atoms in the acetylene, and have the composition indicated by the formulas Ag_2C_2 and Cu_2C_2, respectively. In these cases the acetylene conducts itself like a weak dibasic acid.

As the behavior of acetylene in forming these compounds is that of an acid, it might be expected that it would exhibit, at least to some extent, the conductivity phenomena shown by that class of substances. It appeared, therefore, that the investigation of the molecular conductivity of acetylene might be of interest.

For the cuprous acetylide, from which the acetylene was obtained, we are indebted to Prof. Keiser. The acetylene was liberated from the cuprous acetylide by heating it in a flask, on the water-bath, with a solution of potassium cyanide, as directed by Keiser. The gas was passed into water, which had been redistilled from acid and alkaline potassium permanganate and condensed in a tube of block tin. The conductivity of the water used was determined and found to be negligible. This solution was tested for cyanogen, which might have passed over in some way, by boiling a portion of it with an alkali and ferrous sulphate, neutralizing the alkali with an acid, and adding a ferric salt. No trace of a blue color was obtained. The usual tests for copper, with ammonia or ammonium sulphide also gave negative results, thus showing the absence of all possible impurities. Solutions of

[1] Solutions were prepared by Jones; the conductivity measurements were made by Allen.

[2] This JOURNAL, **14**, 285 and **15**, 535.

acetylene thus prepared and tested were used in the conductivity determinations.

Soon after the work was begun it was found that the solutions gave off the acetylene gas very rapidly, even in glass-stoppered bottles, and at temperatures only a little above zero. It was impossible to retain even dilute solutions at a constant concentration for any considerable time. After a number of trials, the following method was adopted as introducing the least error. The thermostat-bath of the Kohlrausch–Ostwald conductivity apparatus was replaced by a vessel containing much finely powdered ice and a little water, giving a temperature which was approximately zero. The acetylene solution of unknown concentration, was cooled nearly to zero by placing it in a glass-stoppered bottle and immersing the bottle in a freezing-mixture. A portion of this solution was then poured into the resistance cell, (which was already in the ice-bath described above), and the position of equilibrium on the bridge determined as rapidly as possible. A known volume of the solution in the cell was then at once drawn off in a pipette, and the amount of acetylene present determined as follows: A standard tenth-normal solution of silver nitrate and an exactly equivalent solution of potassium chloride were used. The gas was brought into combination by running in an excess of the silver nitrate solution. An equal volume of the potassium chloride solution was then run in, a few drops of a solution of potassium chromate, serving as an indicator, added, and the excess of potassium chloride titrated with the silver nitrate. As there was no loss of acetylene from the solution after the first addition of silver nitrate, the only loss of gas, affecting the results was that which took place during the interval between the conductivity measurement and the first addition of silver nitrate, which was, on an average, only two or three minutes. Since the solutions of acetylene were very dilute and the analyses, of necessity, made with a comparatively small volume, the standardization of the solutions must be regarded as only roughly approximate. The results of the conductivity measurements of the acetylene solutions, are given in the following table. The column headed v gives the volume in liters, which contains a one-

half gram-molecular weight of the gas; μ_v are the molecular conductivities at the volumes v.

	v.	μv.
1.	417	29.0
2.	833	41.0
3.	1111	50.0
4.	2502	77.0

Although these results are necessarily affected by considerable error, due to the causes indicated above, yet they undoubtedly show that solutions of acetylene in water are somewhat dissociated, and that this dissociation increases with the dilution, results which would be expected from the weakly acid character of the compound.

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THE USE OF PHENOLPHTHALEÏN IN ILLUSTRATING THE DISSOCIATING ACTION OF WATER.

BY HARRY C. JONES AND CHARLES R. ALLEN.

The fact that an alcoholic solution of phenolphthaleïn is not colored red by ammonia or triethylamine, but is so colored by potassium, sodium, or barium hydroxide was observed by Menschutkin.[1] He stated that if phenolphthaleïn is added to alcohol, it does not show an alkaline reaction on the addition of triethylamine or ammonia, and he concluded that "the alkalinity of the triethylamine had disappeared, alcohol decomposing the compound of phenolphthaleïn with triethyamine, even when the latter is present in a large excess.

Without knowing of this work of Menschutkin, we observed facts of the same kind in connection with an investigation which is being carried out in this laboratory by Mr. Mackay. Not only an alcoholic solution of ammonia did not show an alkaline reaction with phenolphthaleïn, but when a few drops of a water solution of ammonia were added to several cubic centimeters of alcohol, this solution also failed to give an alkaline reaction with alcoholic phenolphthaleïn. If, however, a considerable volume of water was added to this solution the red color appeared.

[1] Ber. d. chem. Ges., **16**, 315.

When potassium or sodium hydroxide was substituted for ammonia the red color appeared at once, without the addition of water, as stated by Menschutkin. There is thus a marked difference between the action of sodium and potassium hydroxides on the one hand, and that of ammonium hydroxide on the other.

It would be difficult to interpret these facts without the aid of the dissociation theory, unless we were content simply to say that potassium and sodium hydroxides are *stronger* bases than ammonium hydroxide, which really explains nothing. This difficulty becomes the more apparent in that Menschutkin was compelled to seek an explanation in the decomposition of the compound of phenolphthaleïn with triethylamine, by alcohol. In the light of the dissociation theory, however, the facts become intelligible.

In a solution prepared by adding a few drops of aqueous ammonia to several cubic centimeters of alcohol, little or no dissociation of the ammonium hydroxide is effected. The addition of water to this solution dissociates the base, the degree of dissociation depending on the amount of water, with respect to alcohol present. The presence of the ions $\overset{+}{N}H_4$ and $\overset{-}{O}H$, into which the ammonium hydroxide dissociates, will cause the phenolphthaleïn to dissociate into:

$$CO<\begin{matrix}C_6H_4\\O\end{matrix}>\overset{-}{C}<\begin{matrix}C_6H_4O\\C_6H_4OH\end{matrix}+\overset{+}{H} \quad \text{or}$$

$$CO<\begin{matrix}C_6H_4\\O\end{matrix}>C=\begin{matrix}C_6H_4O\\C_6H_4O\end{matrix}+\overset{+}{H}+\overset{+}{H}.$$

The complex anion is colored and gives the characteristic color to the solution in which it is present as an ion. When this colored anion is combined with the colorless cation, hydrogen, to form a molecule, the solution of these molecules is nearly colorless. When the dissociation of the phenolphthaleïn indicated above is effected, its cation $\overset{+}{H}$ would combine with the anion $\overset{-}{O}H$ from the ammonium hydroxide, forming water, since these ions cannot, to any appreciable extent, remain uncombined in the presence of each other.

It may be, however, that the actual course of the reaction is slightly different from that above described, in that the ammonium may, first, combine with the phenolphthaleïn in the alcoholic solution. The addition of water would then dissociate this compound, liberating the colored anion referred to above.[1]

In either case the cause of the color is the presence of the anion,

$$CO<\begin{matrix}C_6H_4\\O\end{matrix}>\overset{-}{C}<\begin{matrix}C_6H_4O\\C_6H_4OH\end{matrix} \quad \text{or} \quad CO<\begin{matrix}C_6H_4\\O\end{matrix}>\overset{=}{C}<\begin{matrix}C_6H_4O\\C_6H_4O\end{matrix},$$

and the dissociation of the compound yielding this colored anion is effected by the water which is present. The dissociation theory furnishes this explanation. It remains to determine whether the explanation is true. If it is, then a solution formed by adding a little aqueous ammonia to a considerable volume of alcohol should show little or no dissociation, and the amount of dissociation should increase with the addition of water. Solutions of potossium or sodium hydroxide in mixtures of alcohol and water should be more dissociated than corresponding solutions of ammonium hydroxide. Indeed, a solution of sodium or potassium hydroxide in alcohol alone, should manifest some dissociation, since, as stated above, it gives the color reaction with phenolphthaleïn.

All of these points can be tested experimentally by the conductivity method. We have carried out such measurements as seemed desirable, and give the results in the following tables. Table I contains the results for ammonium hydroxide. The conductivity of a known volume of a standard solution of aqueous ammonia was at first determined. A measured volume of this solution was then removed, an equal volume of absolute alcohol added, and the conductivity again determined. This process was repeated until nearly all of the water had been removed, the solvent being nearly pure alcohol.

The values under v are the number of liters which would contain a gram molecular weight of the ammonium hydroxide at the particular dilution of the solution used. The column μv gives the molecular conductivities at the volume v

[1] Long (this JOURNAL) **11**, 84, has shown that when strong aqueous ammonia is allowed to set on phenolphthaleïn for a considerable time, phenoldiimidophthaleïn, a colorless substance is apparently formed. If this compound should be formed to some extent in the alcoholic solutions under discussion, its presence would not affect the color reactions of the solutions in question, since it is soluble even in alkalies without color.

and at 25° C. That portion of the solution which was withdrawn in each case after the conductivity reading had been made, was placed in a Nessler tube, treated with some phenolphthalein, and the strength of the red color observed approximately. These observations are recorded in the column headed color. No correction is introduced in the results for the conductivity of the water used, since this was tested, and for water which had been redistilled from acid and alkaline permanganate, was so slight that it was quite negligible.

The corresponding measurements for potassium hydroxide are given in table II.

Table I.

v.	μ_v.	Parts water.	Parts alcohol.	Color.
11	4.8	100	0	strong
22	2.2	50	50	slight
44	1.0	25	75	none, or trace
88	1.1	12.5	87.5	none

Table II.

v.	μ_v.	Parts water.	Parts alcohol.	Color.
8.8	214	100	0	strong
17.6	77	50	50	"
35.2	26	25	75	"
70.4	20	12.5	87.5	"

The conductivity of a standardized solution of potassium hydroxide in pure alcohol alone, was determined with the following results:

v.	μ_v.	Color.
8	15	strong.

The appearance of the red color when water is gradually added to an alcoholic solution of phenolphthalein containing ammonia is not sudden. As the results show, it requires the addition of a considerable volume of water before any trace of red can be detected, then a delicate pink color appears, gradually shading off into red, in the presence of more and more water. This would also be expected, if the color is a function of the dissociation, since the latter increases gradually with the increase in the water present. The results thus appear to confirm at all points the deductions from the dissociation theory.

This experiment furnishes a very satisfactory lecture demonstration of the dissociating action of water. A few drops of an alcoholic solution of phenolphthaleïn are placed in a glass cylinder and diluted to, say 50 cc., by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red color may appear where the aqueous ammonia first comes in contact with the alcoholic phenolphthaleïn, but this will disappear instantly on shaking the cylinder, leaving the solution with a yellowish tint, possibly due to the formation of the ammonium salt of phenolphthaleïn. Water is then gradually added to the cylinder, when the red color appears, first faint, then stronger as the amount of water increases. When the red color has become intense, add a considerable volume of alcohol and the entire color will disappear, leaving a solution which is slightly yellow. The experiment serves then not only to illustrate the dissociating action of water, but also the driving back of the ions into molecules by alcohol.

CHEMICAL LABORATORY.
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Contribution from the Sheffield Laboratory of Yale University.

THE ACTION OF ACID CHLORIDES ON THE SILVER SALTS OF THE ANILIDES.

BY H. L. WHEELER AND B. B. BOLTWOOD.

In this paper we shall describe the action of benzoyl chloride on silver formanilide, on silver 2-4, dichlorformanilide and on silver formorthotoluide. We shall show that these reactions resulted in the formation of diacid anilides and a diacid toluide, and that these diacid derivatives have the structure represented by the general formula $R-N<^{CHO}_{COC_6H_5}$.

Some experiments on the action of chlorcarbonic ethylester on the silver salts of formanilide and formorthotoluide are also given.

If the reactions with benzoyl chloride are viewed as direct double decompositions, the following general equation will represent the formation of the diacid anilides, provided the silver salts have the metal joined to nitrogen:

$$R-N\begin{cases}CHO\\ Ag+Cl\end{cases} COC_6H_5 = R-N<\begin{matrix}CHO\\ COC_6H_5\end{matrix} + AgCl.$$

This view seems to be confirmed by the action of alkali or acids on the diacid anilides and toluide. This action consists in the removal of the formyl group, leaving the benzoyl radical attached to the $R-N<^{H}$ group, and shows that the structure of the diacid anilides is best represented by the formula used above. It may be represented by the following equation:

$$R-N\begin{cases}CHO+HOH\\ COC_6H_5\end{cases} = R-N\begin{matrix}H\\ COC_6H_5\end{matrix} + HOCHO.$$

On the other hand, if the diacid anilides were oxygen derivatives, and if they had the structure

$$R-N=C\begin{matrix}H\\ O.COC_6H_5\end{matrix},$$

corresponding to the pseudoform of the anilide, it would be difficult to see how the formyl group could be removed, leaving the benzoyl radical attached to the group $R-N\begin{matrix}H\\ \end{matrix}$, as shown above.

From the above considerations, we are led to believe that the diacid anilides are nitrogen derivatives. It follows then that the silver salts of the anilides behave with benzoyl chloride as if they had the structure $R-N\begin{matrix}CHO\\ Ag\end{matrix}$, that is, as if the silver was joined to nitrogen. This behavior is remarkable, since the results obtained by the study of the action of alkyl halides on these salts are in direct opposition to this view. The work of Comstock,[1] with Kleeburg,[2] Wheeler[3] and Clapp[4] has shown that these salts give imido ethers with alkyl halides. It was therefore concluded that the silver in these compounds is joined to oxygen, their structure being represented by the formula $R-N=C\begin{matrix}H\\ OAg\end{matrix}$ and the gen-

[1] Ber. d. chem. Ges., **23**, 2274. [2] This JOURNAL, **12**, 493.
[3] *Ibid*, **13**, 514. [4] *Ibid*, **13**, 525.

eral reaction represented as a direct double decomposition as follows:

$$R-N=C\begin{matrix}H\\O\end{matrix}Ag + I\,CH_3 = RN=C\begin{matrix}H\\OCH_3\end{matrix} + AgI.$$

It is not our intention to discuss in this article the probable structure of the silver salts, but to call attention to the fact that these salts react as if they were derivatives of both the normal and pseudoform of the anilide. In other words, if we consider the double decomposition or substitution theory alone, these salts behave as if they had two structures. Questions of this nature, of so-called tautomeric reactions have received considerable attention from Nef[1] and his co-workers in recent years. Nef has plainly shown in his series of elaborate researches on tautomerism that reactions of this nature involve not alone a double decomposition or substitution, but also an intermediate addition. We refer especially to his last article on this subject,[2] and also to his work published in 1892, where he refers to the different behavior of the sodium and silver salts of the anilides with alkyl halides, and decides that it is very improbable that these salts differ in their constitution, and that, in one case, an addition must take place.[3]

It is now evident that although in the action of alkyl halides or of acid chlorides on the silver salts, a double decomposition may take place, such cannot be the case in both. Evidently in one case, and possibly in both an intermediate addition is involved. The experimental evidence thus far obtained, indicates that in the reactions described in this paper, the acid chloride first forms an addition-product with the silver salt. This addition-product then separates silver chloride with the formation of the diacid anilide. That a silver salt can add hydrogen chloride and hydrogen sulphide without immediate separation of silver chloride or sulphide has been shown in the beautiful work of Nef on silver fulminate.[4] The addition of benzoyl chloride to the silver salts of the anilides seem to be another example of this peculiar union.

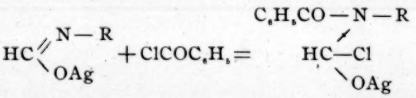
[1] This JOURNAL, **11**, 1; **12**, 379; **13**, 422. J. prakt. Chem. [2], **42**, 161. Ann. Chem. (Liebig), **266**, 52; *Ibid.*, **270**, 267; *Ibid.*, **276**, 900; *Ibid.*, **277**, 59 and 162; *Ibid.*, **280**, 263 and 291.

[2] Ann. Chem. (Liebig), **287**, 269.

[3] Proc. Amer. Acad., May, 1892, 102; and Ann. Chem. (Liebig), **270**, 293.

[4] Ann. Chem. (Liebig), **280**, 313.

If this is indeed the case, it does not necessarily favor the assumption that the silver salts of the anilides are derivatives of the pseudoform of the anilide, nor that addition takes place as follows:



For it is to be noticed that the addition of acid chloride to a silver salt of an anilide might well take place to the nitrogen entirely, the resulting product then being analogous to the hypochlorous acid addition first noticed by Witt,[1] and also to the salts of the anilides with the halogen acids.[2] The compounds being pentavalent nitrogen derivatives as follows:[3]

That the structure of the silver salts of the anilides can not be decided by their final reaction-products is shown by the above considerations, and it is again shown in the work that we have done so far with chlorcarbonic ethyl ester and silver formanilide. We shall show in the latter part of this paper that these substances gave both the oxygen derivative, phenylformimidoethyl ether or ethylisoformanilide, and the nitrogen compound formylphenylurethane from which we isolated phenylurethane. The action with silver formorthotoluide appears to be similar.

Work on the action of acid chlorides on other salts of the anilides is now in progress in this laboratory, and it is also intended to continue the present work on the silver salts, this having been interrupted by the departure of one of us from this laboratory.

[1] Ber. d. chem. Ges., **8**, 1226.

[2] Knorr: Ann. Chem. (Liebig), **245**, 375; Wheeler and Walden: This JOURNAL, **18**, 87.

[3] Pictet explains the formation of benzanilide from benzoyl chloride and formor acetanilide, etc., by means of a similar addition of the acid chloride to the anilide. Ber. d. chem. Ges., **23**, 3011.

Experimental Part.

Formylbenzanilide, $C_6H_5N\begin{matrix}\diagup CHO \\ \diagdown COC_6H_5\end{matrix}$. — When dry silver formanilide[1] is suspended in a small amount of benzene and one molecular proportion of benzoyl chloride is added, the first evidence of a reaction begins with a slight warming. On stirring, the mass thickens until it becomes almost semi-solid, it then becomes more fluid and the odor of benzoyl chloride disappears. The action can be hastened by warming. On filtering and concentrating the benzene solution, silver chloride frequently separates, although the extract filters at first perfectly clear. The residue consists of an oil which on standing solidifies. When this mass is crystallized from alcohol, more silver chloride separates along with beautiful colorless needles of the diacid anilide. It sometimes takes several crystallizations from alcohol to free these crystals completely from silver. Attempts were made to isolate this supposed addition product which apparently is formed here, and which would explain the persistency with which silver chloride contaminates the product, but the reaction took place too rapidly to permit of the isolation of an addition-product suitable for analysis, even at the melting-point of benzene. The yield of formylbenzanilide is practically quantitative. Analysis of the diacid anilide dried over calcium chloride gave:

	Found.	Calculated for $C_{14}H_{11}NO_3$.
C	74.33	74.67
H	4.92	4.88
N	6.46	6.14

Formylbenzanilide is readily soluble in benzene and chloroform, less so in ether and alcohol, and difficultly in water. It melts at 112°. When it is treated with sodium hydroxide the formyl group is removed and benzanilide melting at 162° is obtained. A mixture of benzanilide and formylbenzanilide can readily be distinguished when crystallized from alcohol. The former separates at first in needles, the latter forms a supersaturated solution, and on shaking deposits plates.

2-4 Dichlorformanilide, $C_6H_3Cl_2NH.CHO$.—This was pre-

[1] This was prepared according to the directions of Comstock and Kleeburg, *loc. cit.*

pared from acetanilide by chlorinating according to the method of Beilstein and Kurbatow.[1] From the pure dichloracetanilide thus obtained the acetyl group was replaced by the formyl in the usual manner. 2-4 dichlorformanilide crystallizes from alcohol in colorless needles, which melt at 153°.

	Found.	Calculated for $C_7H_5NOCl_2$.
C	44.15	44.22
H	2.71	2.63

Silver 2-4 Dichlorformanilide, $C_6H_3Cl_2NAgCHO$, was obtained from the sodium salt in the same manner as silver formanilide. It separates as a white amorphous bulky precipitate, and as regards the action of light, it is the most stable silver salt of the anilides that we are familiar with. It was washed with water and dried over sulphuric acid.

	Found.	Calculated for $C_6H_3Cl_2NAgCHO$.
Ag	36.48	36.36

2-4 Dichlorformylbenzanilide, $C_6H_3Cl_2N\begin{matrix}\nearrow CHO \\ \searrow COC_6H_5\end{matrix}$.—To prepare this, the above silver salt was mixed with benzoyl chloride in proportion to their molecular weights, the operation being carried out as before in dry benzene. When the benzene solution was filtered and evaporated, an oil remained. This was taken up in 95 per cent. alcohol. This left a residue apparently of silver chloride. On letting the alcoholic solution stand, more silver chloride separated; then the diacid anilide, first as an oil, and finally in bunches of colorless acicular prisms. These, on crystallizing from alcohol, melted at 77°. Analysis gave:

	Found.	Calculated for $C_{14}H_9Cl_2NO_2$.
C	57.09	57.14
H	3.17	3.06
N	4.83	4.76

2-4 Dichlorformylbenzanilide is readily soluble in benzene and in hot alcohol, but difficultly soluble in water.

2-4 Dichlorbenzanilide, $C_6H_3Cl_2N\begin{matrix}\nearrow H \\ \searrow COC_6H_5\end{matrix}$.—This was

[1] Ann. Chem. (Liebig), 196, 215.

formed when 2-4 dichlorformylbenzanilide was boiled with dilute hydrochloric acid, the resulting product was crystallized from strong alcohol. It melted sharply at 117°. Analysis gave:

	Found.	Calculated for $C_{13}H_9NOCl_2$.
N	5.11	5.26

2-4 Dichlorbenzanilide is only sparingly soluble in hot water, difficultly in cold alcohol, readily in hot, and easily in ether.

Formylbenzorthotoluide, $C_6H_4CH_3N\begin{matrix}CHO\\COC_6H_5\end{matrix}$. — The preparation of this from silver formorthotoluide and benzoyl chloride was precisely the same as we have described in the two preceding cases. The product showed the same tendency to retain silver. It was obtained from the benzene solution as an oil. This was dissolved in alcohol and the solution allowed to stand, when beautiful, thick, apparently rectangular plates, diagonally striated, separated. These on crystallizing from alcohol melted at 92°. Analysis gave:

	Found.	Calculated for $C_{15}H_{13}NO_2$.
C	75.12	75.31
H	5.64	5.43
N	5.87	5.85

Formylbenzorthotoluide is readily soluble in benzene and in warm alcohol, but difficultly soluble in water. Some of the analyzed material was treated with dilute sodium hydroxide, and the product then crystallized from dilute alcohol, when benzorthotoluide was obtained in colorless needles melting at 142°.

A comparison of the melting-points of the diacid derivatives, described in this paper, with those of the mono acid anilides and toluides shows no strict regularity, except that the melting-points of the di-derivatives are lower than those of the benzoyl compounds. This will be seen from the following list:

	M. P.		M. P.
Formanilide	46°.	Formorthotoluide	62°.
Formylbenzanilide	112°.	Formylbenzorthotoluide	92°.
Benzanilide	163°.	Benzorthotoluide	142°.

	M. P.
2-4 Dichlorformanilide	153°.
2-4 Dichlorformylbenzanilide	77°.
2-4 Dichlorbenzanilide	117°.

Action of Chlorcarbonic Ethylester on Silver Formanilide and on Silver Formtoluide.

Silver formanilide and chlorcarbonic ester were mixed in benzene solution in molecular proportions; the reaction took place rapidly and carbonic acid gas was given off. To complete the reaction, the whole was warmed on the water-bath. On filtering from silver chloride and evaporating the benzene solution, an oil was obtained; this was distilled at a pressure of 18 mm., when a small amount of phenylformimidoethyl ester or ethylisoformanilide[1] was obtained, which boiled at about 106° under these conditions. This substance was identified by its action with aniline, and also on standing alone exposed to the air. In both cases diphenylformamidine was obtained, melting at 136°. For comparison this imidoether was made from the silver salt of formanilide with ethyl iodide. This product was found to be identical with that obtained from the chlorcarbonic ester reaction.

Phenyl 2-4 dichlorphenylformamidine, $HC\begin{matrix}=NC_6H_5\\ \diagdown NHC_6H_3Cl_2\end{matrix}$.—This was formed when the above imidoether was mixed with 2-4 dichloraniline. It crystallizes from benzene in bunches of minute colorless plates, which melt at 159°.

	Found.	Calculated for $C_{13}H_{10}N_2Cl_2$.
N	10.59	10.57

The residue left after the distillation of the imido ether was treated with dilute hydrochloric acid and alkali, and then crystallized from ligroïn. This gave phenylurethane melting at 52°. On extracting the silver chloride residue with water, diphenylformamidine hydrochloride was obtained.

In another experiment 30 grams of silver salt were taken, and an excess of chlorcarbonic ester was unintentionally used. In this experiment we succeeded in isolating phenylurethane in addition to the imido ether and the amidine. The approxi-

[1] Described by Comstock and Clapp, *loc. cit.*

mate quantities of these substances formed were as follows: 0.9 gram of diphenylformamidine hydrochloride, 5.0 grams of imido ether and 14 grams of oil, which we did not succeed in purifying. A small quantity of isonitril was formed, probably in the distillation. The oil evidently consisted of the expected formylphenyl urethane, since, on warming with dilute sodium hydroxide and then crystallizing the product from ligroïn, phenylurethane was obtained, melting at 52°. The latter was positively identified by analysis:

	Found.	Calculated for $C_9H_{11}NO_2$.
C	65.60	65.45
H	6.74	6.66

Experiments with the silver salt of formorthotoluide and chlorcarbonic ethyl ester, conducted in the same manner as the preceding, gave orthotolylformimidoethyl ester, *s*-ditolyl urea, and a residue, presumably formyltolyl urethane, but we did not succeed in purifying this for analysis.

Orthotolylformimidoethyl Ester, $C_6H_4CH_3N=C\begin{matrix}H\\ OC_2H_5\end{matrix}$—

This is an aromatic oil boiling at 101°, at 12 mm. pressure. Analysis gave:

	Found.	Calculated for $C_{10}H_{13}NO$.
C	73.19	73.62
H	7.94	7.91

From the high-boiling fractions of the imido ether a crystalline colorless substance separated. This was washed with ligroïn and analyzed.

	Found.	Calculated for $C_{15}H_{16}N_2O$.
C	74.44	74.37
H	7.11	7.43
N	11.06	11.57

Its melting-point, 256°, and the above analysis show that this substance was *s*-orthoditolyl urea.

Contribution from the Sheffield Laboratory of Yale University.

ON THE EXISTENCE OF TWO ORTHOPHTHALIC ACIDS.

By W. T. H. Howe.

INTRODUCTION.

The melting-point of orthophthalic acid, as given by different investigators, varies from 175° to 213°. Lossen[1] obtained phthalic acid by oxidizing naphthalene with potassium permanganate and determined the melting at 184°. Weith[2] obtained, by oxidizing orthotoluic acid, an acid crystallizing in colorless prisms and melting from 182° to 195°. Piccard[3] obtained phthalic acid from the same source, but gave as its melting-point 180°, while Carius[4] gave the melting-point as low as 175°–180°. Ador[5] declared these melting-points as too low, since phthalic acid obtained by boiling the anhydride with water gave 203° for the finely pulverized, and 213° for the crystallized acid, although he says that the acid precipitated from its salts apparently does melt at 180°. Graebe,[6] in a revision of the previous work, assumed that the higher melting-points given by Ador were due to too rapid heating, and that the 184 degree melting-point of Lossen was the correct one.

The present investigation has shown that two orthophthalic acids exist, one melting at 184°, the other at 203°. The variations in melting-point found by previous observers have, therefore, been due, not alone to the formation of the low melting anhydride, but to the fact that under the varying conditions of preparation, these two different acids have been obtained or mixtures of them. Very probably, certain low melting-points have been due to an admixture of an acid salt which is precipitated together with the acid under certain conditions of concentration.

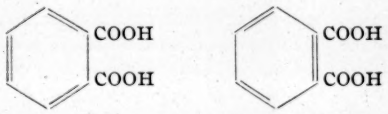
The acid melting at 203° will be called the α-acid, while that melting at 184° will be designated as the β-compound. The higher melting-point has usually been the accepted one.

The two acids are identical in composition, molecular weight and molecular refraction, but they differ (1) in melt-

[1] Ann. Chem. (Liebig), **144**, 78.
[2] Ber. d. chem. Ges., **7**, 1057.
[3] Ber. d. chem. Ges., **19**, 579.
[4] Ann. Chem. (Liebig), **148**, 62.
[5] Ann. Chem. Liebig), **164**, 230.
[6] Ann. Chem. (Liebig), **238**, 321.

ing-points, (2) in electrical conductivity, (3) in solubility, (4) in the properties of their salts with organic and inorganic bases, (5) in their reduction products. The β-acid is converted into the α-body simply by boiling with water, while the reverse change takes place by the action of strong acids or alkalies.

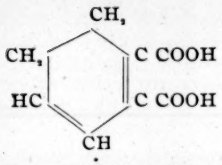
It is possible to explain the existence of two orthophthalic acids by the single and double bond isomerism required by Kekulè's benzene formula, as follows :



The existence of this form of isomerism has never been definitely established, and indeed its absence has been considered as a strong argument against Kekulé's formula, but it seems possible from the analogous behavior of citra- and itaconic acids, which are believed to have single and double bonds between the carbons to which the carboxyls are attached, thus :

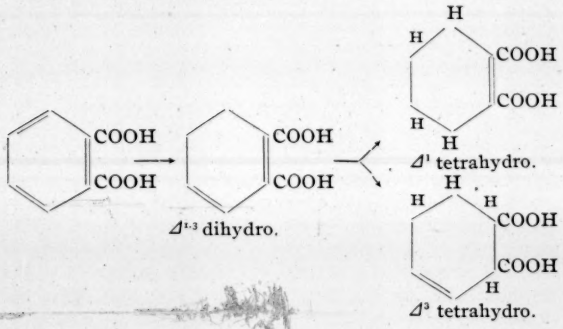
Furthermore, the single and double bond isomerism is plausible from the behavior of the β-acid on reduction as compared with that of the α-acid as studied by Baeyer.[1] The β-acid yields a new dihydrophthalic acid when reduced under the same conditions as used by Baeyer with the α-acid.[1] This product is much more unstable than the $\Delta^{3,5}$ body obtained by Baeyer from the α-acid. It differs from that compound by reducing a cold silver nitrate solution and by being reduced by sodium amalgam at a low temperature to two tetrahydro-orthophthalic acids. Upon the basis of Baeyer's exhaustive work, the new dihydro acid seems to be the $\Delta^{1,3}$ compound,

[1] Ann. Chem. Liebig, **269**.



this being the only one, previously unknown, considered by Baeyer as stable enough to exist, and he predicted that this would be rather unstable.

Of the two tetrahydro acids obtained from the reduction of the new dihydro acid, one agrees in its melting-point and that of its anhydride, as well as in its solubility with the Δ^1 compound obtained by an indirect process by Baeyer, and it is doubtless that compound. The other is a new tetrahydro acid, and since, according to Baeyer's theory, only the cis and trans Δ^3 compounds have been lacking, this should be one of those acids. If this proves to be the case, the double bond should occur between the carboxyls in the β-acid, as may be seen from the following formulæ:

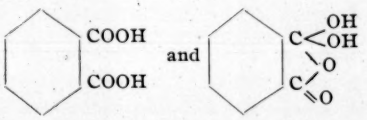


It is an important fact that Baeyer did not obtain the Δ^1 tetrahydro acid by the direct reduction of any dihydro compound, because it shows a marked difference in the behavior

[1] The β-acid yields a new dihydrophthalic acid when reduced under the same conditions as used by Baeyer with the α-acid.

of the β-orthophthalic acid, and shows the probable position of the double bond.

Other explanations of the existence of two orthophthalic acids seem less satisfactory than the one according to Kekulè's formula suggested above. An isomerism depending upon the symmetrical and asymmetrical arrangement of the hydroxyls, as follows:



has the arguments against it that the second form would apparently be very unstable, and moreover, the identical molecular refraction of the two isomers does not allow of this assumption.

EXPERIMENTAL PART.

Method for Preparing the Two Acids in a Pure Condition.

α-Orthophthalic Acid.—Commercial phthalic acid is usually a mixture of the two acids, but if an aqueous solution of it or of the anhydride, be boiled for 3 to 4 hours, an acid crystallizes out on cooling, which, filtered and dried for an hour at 100°, melts in a finely pulverized condition at 203–4°. It was shown by Graebe that if the bath be kept at 183–4° for some time the acid melts. But this is due simply to the decomposition of the acid into its anhydride. This may be effected at as low a temperature as 160°.

To prepare the pure β-acid, the anhydride is dissolved in cold dilute sodium hydroxide, the solution cooled to 0°, slowly precipitated with hydrochloric acid and dried over sulphuric acid. Phthalic anhydride appears to be the anhydride of the β-acid, for it yields this on dissolving in alkali, precipitating and drying as stated above. This cannot be due to the isomerizing influence of the alkali, since the pure α-acid, dissolved in alkali, precipitated at 0° and dried over sulphuric acid, melts at 199–201°. Furthermore, the anhydride reduced with zinc dust and acetic acid according to Wislicenus[1] yields

[1] Ber. d. chem. Ges., 17, 2180.

the same hydrodiphthalyl as obtained in the present work by the reduction of the β-acid.

The α-acid is converted into the β-isomer by boiling with a 30 per cent. sodium or potassium hydroxide solution for four to five hours, then precipitating and drying as mentioned above. Strong acids also partially change the α- into the β-acid.

The β-acid is extremely sensitive to warm water and readily changes in part into the ordinary acid. This may be caused even by the heat generated in precipitating the acid at ordinary temperatures from its alkali salt solutions, and the slightly moist acid cannot be dried at 80° without a considerable change taking place. Thus, the β-acid, precipitated from its sodium salt solutions and dried at 80°, melted at 184–195°, but precipitated at 0° and dried over sulphuric acid, it melted at 183–4°. To effect a complete change, however, of the β into the α-acid, three to four hours boiling is required as stated above.

Light seems to have no effect upon the β-acid, moist or dry, since two portions of the same preparation, one dried in the dark, the other exposed to sunlight, both melted at 184°.

Melting-points lower than that of the β-acid, such as 175–180°, observed by previous investigators, as noticed above, appear to have been due to an inter-mixture of an acid salt with the acid. The pure β-acid is precipitated by acidifying dilute solutions, but from concentrated alkaline solutions a white crystalline precipitate is thrown down. This is identical in appearance with the pure acid, but it melts at 175–180°, and upon drying and extracting with absolute alcohol, a residue of an acid salt remains.

Analytical results for the two orthophthalic acids :

	Calculated for $C_8H_6O_4$.	Found. α-acid.	Found. β-acid.
C	57.84	57.38	57.42
H	3.62	3.86	3.82

The molecular weights were determined by Beckmann's method in absolute alcohol solution :

α-Orthophthalic Acid.

Weight of solution	17.5119 grams.
" " "	1.2364 "
Rise of boiling-point	0.49 "
Molecular rise for alcohol	11°.5

Molecular weight = 165.4.

β-Orthophthalic Acid.

Weight of solution	23.7301 grams.
" " "	1.2369 "
Rise in boiling-point	0.365 "
Molecular rise for alcohol	11°.5

Molecular weight = 164.

Molecular weight calculated for $C_8H_6O_4 = 166$.

Molecular refraction:

	Obtained.	Calculated by Ostwald.
α-Orthophthalic acid	40.42 40.79	39.26
β- " "	40.47	39.26

The *electrical conductivity* for the α-acid was determined by Ostwald,[1] as follows:

v.	μ.	100 M.	100 K.
64	85.9	24.3	0.121
128	114.2	32.3	0.121

In the present work the following results were obtained for the same acid:

v.	μ.	100 M.	100 K.
18.5	49.07	13.87	0.121
37.0	67.33	19.02	0.121
74.0	90.95	25.69	0.120

The greater conductivity of the β-acid as follows shows it to be the stronger of the two:

v.	μ.	100 M.	100 K.
23.63	58.29	16.46	0.137
47.3	78.00	22.04	0.137

$\mu\infty = 354$.

[1] Ztschr. phys. Chem., 3, 376.

The Relative Solubilities of α- and β-Orthophthalic Acids, Determined according to V. Meyer's Method in Absolute Alcohol.

α-Orthophthalic Acid.

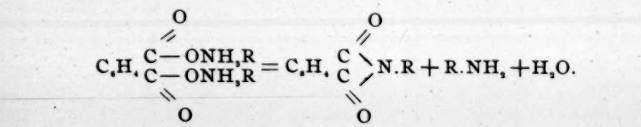
At 20°, 100 parts of solvent dissolved 11.74 parts acid.
" 23° " " " " " 14.08 " "

β-Orthophthalic Acid.

At 20°, 100 parts solvent dissolved 14.12 parts acid.
" 23° " " " " " 16.18 " "

To avoid the tendency of alcohol to isomerize the β- into the α-acid, great care was used in not heating too long or much above the temperature for determination.

Salts with Organic Bases.—The aniline, naphthylamine and quinoline salts of both the acids were prepared by adding to the alcoholic solution of the acid the calculated quantity of the base. Warm alcohol or an excess of the base quickly changes the salt of the β- to that of the α-acid. In a dry condition the salts of the β-acid are perfectly stable, and furthermore, can be boiled in a benzene solution for several hours without effecting any change. If, however, an alcoholic solution of the aniline or naphthylamine salts of either the α- or β-acid be boiled for six or eight hours, water and the free base split off and phenyl or naphthylphthalimide is obtained. Thus:



To prepare the *brucine salts* the calculated quantity for two molecules of brucine was dissolved in dry benzene, and one molecule of α- or β-acid added. On cooling, the α-salt crystallized out in beautiful, doubly-terminated prisms, the β-salt in clusters of needles. By recrystallizing the β-salt several times from hot alcohol the pure brucine salt of the α-acid is obtained.

A Comparison of the Salts of the Two Phthalic Acids.

	α-Orthophthalic Acid.	*β-Orthophthalic Acid.*
Aniline,	plates M. P. 160°	plates M.P. 147–8°
α-Naphthylamine,	doubly terminated prisms M. P. 163°	needles M.P. 155°
Quinoline,	plates M. P. 98	needles M. P. 92°
Brucine	brilliant, doubly-terminated prisms, M.P. 228°	needles M.P. 212-3°

The aniline salt is the only one previously known. This was obtained by Beamer and Clarke,[1] and melted at 145–6°. This was undoubtedly the β-salt, although no source or method of preparation for the acid was given :

Analytical Results.

Aniline salts :

	Calculated for $C_{20}H_{20}N_2O_4$.	Found. α-salt.	Found. β-salt.
C	66.30	65.92	66.01
H	5.53	5.72	5.63

α-Naphthylamine salts :

	Calculated for $C_{28}H_{24}N_2O_4$.	Found. α-salt.	Found. β-salt.
C	73.34	74.22	74.15
H	5.21	5.42	5.51

Quinoline salts :

	Calculated for $C_{28}H_{28}N_2O_4$.	Found. α-salt.	Found. β-acid.
C	73.57	73.13	73.28
H	4.71	4.86	4.93

Brucine salts :

	Calculated for $C_{54}H_{58}N_4O_{12}$.	Found. α-acid.	Found. β-acid.
C	78.81	72.22	72.35
H	6.52	6.82	6.89

Reduction of β-Orthophthalic Acid.

The β-acid was submitted to reduction under the following conditions : 20 grams of acid and 32.8 grams of sodium acetate were dissolved in 200 cc. of water, and while cooled with ice and constantly stirred, 400 grams of 3 per cent. so-

[1] Ber. d. chem. Ges., **12**, 1066.

dium amalgam were added, 40 grams at a time, and each time 6 cc. of 50 per cent. acetic acid. The solution was thus kept acid throughout the operation, and at no time did the temperature rise above 6°. After the reduction was completed, sodium sulphate was separated by the addition of 50 cc. of dilute sulphuric acid and an acid was precipitated by acidifying with dilute sulphuric acid, which crystallized repeatedly from hot water, with the addition of animal charcoal, separated in colorless prisms, melting at 195°. Dried at a constant weight over sulphuric acid, the compound gave analytical numbers for a dihydrophthalic acid.

	Calculated for $C_8H_8O_4$.	Found. I.	II.
C	57.14	57.20	56.92
H	4.76	4.88	4.93

For the preparation of the anhydride, the finely pulverized dihydro acid was treated with ten times its volume of acetic anhydride and permitted to stand for twenty-four hours, when solution occurred. Upon evaporating the solution in a vacuum over soda-lime, the anhydride crystallized out in long needles, which purified from benzene or chloroform, melted at 126°. The anhydride dissolved in hot water regenerated the original acid.

Under the same conditions, Baeyer obtained from α-orthophthalic acid, a dihydro acid with a melting-point of 210°, and its anhydride melting at 101-3°, while the new dihydro acid melts at 195° and its anhydride at 126°. Furthermore, the new dihydro acid showed decided chemical differences from the $\Delta^{3,5}$ dihydro compound obtained from the α-orthophthalic acid. The new dihydro acid instantly reduces a silver nitrate solution in the cold, while for the $\Delta^{3,5}$ acid to act, warming on the water-bath is required. The new dihydro acid is readily reduced in the cold to two tetrahydro acids, while the $\Delta^{3,5}$ acid is not acted on under such conditions. Furthermore, on boiling the two dihydro acids with copper acetate, the new acid precipitates cuprous oxide, while the $\Delta^{3,5}$ requires the addition of acetic acid to effect such a reaction. The above differences may be tabulated as follows :

	$\Delta^{3,5}$ *Acid.*	*New Dihydro Acid.*
M. P.	210°	195°
M. P. of anhydride	101–3°	126°
Toward cold solution of $AgNO_3$	no reaction	reduces
Toward sodium amalgam in cold	no reaction	reduces to tetrahydro acids
Toward $Cu(C_2H_3O_2)_2$	precipitation of cuprous oxide on addition of acetic acid	precipitation of cuprous oxide without acetic acid

The new dihydro acid behaves identically with the $\Delta^{3,5}$ acid in instantly decolorizing a permanganate solution and in being converted by boiling alkalies into the most stable dihydroorthophthalic acid, $\Delta^{2,6}$.

Reduction of the New Dihydro Orthophthalic Acid.

10 grams of the new dihydro acid were dissolved in 18 grams of sodium acetate and 125 cc. of water. After cooling the solution with ice, a small excess of the calculated amount of 3 per cent. sodium amalgam was added in ten gram portions, and with each addition of amalgam, 3 cc. of 50 per cent. acetic acid. After the amalgam had been added, an acid was isolated, according to the method used with the dihydro compound, which was rather insoluble in cold water and crystallized from hot water in long doubly terminated prisms, melting at 206° with a partial change into its anhydride. The filtrate from the acid melting at 206° yielded a small amount of a very soluble acid, crystallizing in plates, and melting at 120°. This formed an anhydride at the temperature of the water-bath, melting at 78°.

Dried over sulphuric acid the two compounds gave the following analytical results:

	Calculated for $C_8H_{10}O_4$.	Found. I. M. P. 206°.	Found. II. M. P. 120°.
C	56.37	56.24	56.31
H	5.88	6.01	5.90

These analyses show both I and II to be tetrahydrophthalic acids. No. II from its melting-point and that of its anhydride and its easy solubility in water, would seem to be the

Δ^1 tetrahydroorthophthalic acid obtained by Baeyer[1] by an indirect process.

There is no tetrahydrophthalic acid known that agrees with No. I in the melting-point or that of its anhydride. It reduces a silver nitrate solution on warming for some time on the water-bath, and decolorizes a cold potassium permanganate solution. This tetrahydro acid is not acted upon by acetyl chloride, for, upon boiling a portion of the acid with fifteen times its volume of acetyl chloride for an hour, the chloride distilled, leaving the acid unchanged. If, however, the acid be boiled with ten times its volume of acetic anhydride for ten minutes, and evaporated in a vacuum over soda-lime, the anhydride crystalizes out in short needles which recrystallized from chloroform or benzene, melts at 112–3° and regenerates the original acid from hot water.

Baeyer,[2] in his study of the reduction of α-orthophthalic acid, obtained, among his by-products, a compound giving analytical percentages and chemical behavior of hydrodiphthalyl, but melting at 250° instead of 228°, the melting-point assigned by Wislicenus,[3] who first obtained the compound by reducing phthalic anhydride. Later Hasselbach[4] believed the hydrodiphthalyl melting at 228° to be slightly impure, since the compound obtained by him and melting at 250° was perfectly white, while his hydrodiphthalyl, melting at 228°, was always slightly colored.

A hydrodiphthalyl was isolated in the present investigation from the reduction of β-orthophthalic acid. This compound could be obtained perfectly colorless from glacial acetic acid and melted at 228°. On boiling with sodium hydroxide, hydrodiphthalyllactonic acid was obtained, melting at 198°. From this it would seem that there are two hydrodiphthalyls corresponding to the α- and β-orthophthalic acids. The relation between the two is being studied in this laboratory.

Metallic Salts of α- and β-Orthophthalic Acids.—A considerable number of metallic salts of the two orthophthalic acids have been prepared. In many cases they differ in form and in water of crystallization. In every case the α-salt is the

[1] Ann. Chem. (Liebig), **258**, 203.
[2] Ann. Chem. (Liebig), **269**, 155.
[3] Ber. d. chem. Ges. ,**17**, 2180.
[4] Ann. Chem. (Liebig), **243**, 265.

stable one, and the β-salt is converted into this by boiling with water. It is expected that a description of these salts with their crystallographic relations will be given in a future article. Further work also will be done on the reduction products and on the substituted phthalic acids.

It should be stated that the variability in the melting-point of orthophthalic acid, came to the notice of the author while engaged in work under the direction of Dr. F. L. Dunlap at Harvard University in the summer of 1894. Most of the investigation, however, has been carried out in this laboratory.

The author takes pleasure in expressing his thanks to Prof. H. L. Wells of this laboratory for valuable advice, and also to Dr. A. J. Wakeman for assistance in connection with the physical determinations.

THE REDUCTION OF PERMANGANIC ACID BY MANGANESE SUPEROXIDE.

By H. N. Morse, A. J. Hopkins and M. S. Walker.

One finds in the literature of analytical chemistry very contradictory statements regarding the stability of solutions of potassium permanganate, and probably many have noticed that while solutions made from one specimen of the salt may exhibit a gratifying stability, those made from material of different origin decompose with rapidity. Many observations point to the conclusion that this difference is due to the presence or absence of manganese superoxide in the specimens of permanganate from which the solutions are made; in other words, that the decline in concentration results from a reduction of the permanganic acid by the oxide with the evolution of oxygen in the free state.

Experiments designed to test the fact of such reduction and to discover the quantitative relations involved in it have been in progress in this laboratory for several years. During that time hundreds of determinations of manganese and oxygen have been made, and a great mass of evidence has been secured which points to certain well-defined conclusions. This evidence has already been utilized, in part, in theses for the doctor's degree. It is too voluminous to present in detail,

and we shall therefore give only so much of it as may be thought necessary to establish the conclusions arrived at. For the sake of clearness and brevity, we shall also depart from the usual custom by giving the principal conclusions before presenting the evidence on which they are based.

The work upon the reduction of permanganic acid by manganese superoxide has led to the investigation of another question closely related to it, namely the instability of the superoxide itself when prepared in the wet way. But the facts developed in this direction are, in the main, reserved for another paper.

I.

Potassium Permanganate and Permanganic Acid in Solution are Reduced by Precipitated Superoxide of Manganese with Evolution of Free Oxygen.

a. Solutions of permanganate which have been filtered through asbestos are, as a rule, much more stable than the same solutions unfiltered. Again, filtered solutions which remain undisturbed in stoppered bottles are more stable than the same solutions in use. In the latter case, the solutions probably acquire, in consequence of the exposure to which they are subjected, the oxide required for the initiation of the reduction.

b. In solutions of permanganate containing large quantities of suspended oxide, there is often, even at ordinary temperatures, a visible evolution of gas, which gas is found, on examination, to be oxygen. If the temperature of the solution is raised, the evolution of gas becomes more rapid.

c. A solution of permanganate which has once begun to lose strength declines in concentration with increasing rapidity, owing apparently to the increasing quantity of suspended oxide.

d. If a solution in which considerable oxide is suspended is heated to its boiling-point, it loses its color after a time; while a solution of equal concentration which has been filtered through asbestos is only slightly altered under the same conditions. That this change is attended by the loss of oxy-

gen is easily proved by determining the oxidizing power of the solution before and after heating.

e. The following is a form of the above experiment which is frequently employed in this laboratory for the purpose of emphasizing the necessity of keeping standard solutions of permanganate free from suspended oxide, as well as for the purpose of illustrating the need of certain precautions in determining manganese by the method of Volhard.

The relation of a dilute solution of manganese sulphate to a standard solution of potassium permanganate having been determined by the method of Volhard, a measured portion of the former is prepared for precipitation in the usual manner, and to it is added twice the required volume of permanganate. The body of the flask is then immersed in boiling water until the color of the permanganate disappears, after which the total active oxygen remaining in the liquid is determined by means of oxalic acid and permanganate and compared with the quantity introduced. The time required for decolorization is usually from two to five hours, and depends very much upon the exact temperature of the water-bath.

If the remaining oxygen is determined immediately after the disappearance of the color, it is found that quite exactly three-tenths of the total active oxygen in the permanganate has been lost. This relation indicates a reduction of the half of the permanganate which is not concerned in the precipitation of the manganese of the sulphate in accordance with the following equation:

$$2HMnO_4 + MnO_2 = H_2O + 3MnO_2 + 3O.$$

The correctness of the explanation has also been demonstrated by the determination of the oxygen evolved.

If the heating of the flask is continued for some time after the disappearance of the color, the remaining oxygen is found to be somewhat less than that required by the equation, showing that the precipitated oxide also loses oxygen at the temperature of boiling water.

The facts enumerated above are sufficient to demonstrate the very decided reducing action of manganese superoxide on permanganic acid. It appears improbable to us that some of

them should have escaped the notice of analytical chemists, nevertheless we were unable to discover in the available records more than two references to the possibility of such a reduction and these were somewhat obscure. Thenard in 1856,[1] states that manganese dioxide may act upon potassium permanganate either as a reducing agent, in which act the dioxide is converted into a manganate, or its influence may be catalytic causing an evolution of oxygen. Again in 1858,[2] Mulder ascribes the decomposition of permanganate solutions to the presence of potassium manganate. It is certain that the importance of this reduction in its bearings upon the stability of permanganate solutions is not generally appreciated; for nowhere do we find the necessity for the careful filtration of these solutions emphasized. On the other hand, one often finds the deterioration of the solutions ascribed to the dust acquired through exposure to the air. It may safely be asserted that the reduction actually accomplished by dust is insignificant as compared with that accomplished by the oxide produced by the dust.

f. The following experiments are given to illustrate the effect of the presence of suspended oxide upon solutions of potassium permanganate at ordinary temperatures. The oxide used was prepared by pouring a hot dilute solution of manganese sulphate into a hot solution of potassium permanganate. The latter solution contained an excess of the salt and had been acidified with nitric acid. To obtain the oxide in weighable form, it was dried at 65°. We have found that the ratio of oxygen to manganese in oxide precipitated in this way is invariably 2 : 1 if analyzed immediately after the removal of the excess of permanganate and while it is still wet. If, on the other hand, the analysis is delayed for a few hours, or if the oxide is dried at any temperature above that of the air, the proportion of oxygen is found to be smaller. It appears to be impossible for the precipitated oxide to retain the full proportion of oxygen except in the presence of permanganic acid. If, however, an oxide which has lost oxygen by standing or by drying is again placed in a solution of per-

[1] Compt. Rend., **42**, 382. [2] Jahresbericht, p. 581.

manganate, it soon recovers the full amount of the oxygen it has lost.

It might be inferred from these facts, which have often been verified, that the reduction of permanganic acid by the superoxide consists in the simple restoration of the oxygen which the oxide loses spontaneously. The explanation, however, appears to be inadequate, since the oxide, in the absence of permanganic acid, is reduced much more slowly than is the permanganic acid in the presence of the oxide.

It will be seen that in all the experiments described some allowance is to be made for a slight reduction of the permanganate due to the deficit of oxygen in the oxide employed. The reduction from this cause is, however, slight as compared with the total observed reduction.

1. *June 14, 1892.*—Placed 250 cc. of permang nate solution which had been filtered through glass wool in a dark place. Concentration equivalent to 5.278 milligrams of iron per cc.

Oct. 14, 1892.—The solution was analyzed and found to have declined in strength 0.72 per cent.

2. Dates and solution the same as in No. 1. The bottle, however, was kept in mildly diffused light. On analysis the decline in concentration was found to be 0.72 per cent.

3. Dates the same as in Nos. 1 and 2. The solution was filtered through glass and kept in a dark place. Its concentration was equivalent to 14.379 milligrams of iron per cc. On analysis it was found to have lost 1.71 per cent. of the active oxygen.

4. Dates and solution the same as in No. 3. The bottle containing the solution, however, was, like No. 2, kept in mildly diffused light. The loss in strength was 2.41 per cent. The above experiments are not believed to be a satisfactory test of the stability of a permanganate solution which is entirely free from suspended oxide. It is thought, rather, that owing to the imperfect filtration through glass wool, all of the solutions contained traces of suspended oxide. In the subsequent experiments bearing on the stability of pure solutions, greater pains were taken to secure a perfect filter.

5. *Dec. 10, 1892.*—Placed four bottles containing permanga-

nate solution in a dark place. The solutions were filtered with great care through asbestos into the thoroughly cleansed bottles and precautions were taken to prevent contamination from the air during and after filtration. Two of the bottles contained a solution equivalent to 5 milligrams of iron per cc., and the other two a solution having twice that strength. The solution in one of each pair of bottles was examined Dec. 24, 1892, May 31, 1893, Oct. 4, 1893, and March 16, 1894, while the contents of the second bottle of each pair were left undisturbed until March 17, 1894. In no case could any decline in concentration be detected.

6. Experiment No. 5 was paralleled in every particular except one. The solutions were kept in mildly diffused light instead of in darkness. As in the preceding case, all of the solutions were found after fifteen months to have the same strength as when put away.

It appears from Experiments 5 and 6 that carefully filtered and properly protected solutions of permanganate exhibit a high degree of stability. A pure solution may, however, easily become contaminated while in use; it is therefore to be recommended that standard solutions be refiltered from time to time into clean bottles and that the portions left in burettes should never be returned to the main supply without filtration. Such a practice, together with other precautions which readily suggest themselves, renders a frequent redetermination of the concentration of permanganate solutions unnecessary.

It has long been known that direct sunlight exerts a deleterious influence upon solutions of potassium permanganate. The following experiment was undertaken with a view of determining approximately how great that influence may be.

7. *Dec. 10, 1892.*—Place four bottles containing filtered solutions of permanganate in a window facing to the south. The solution in two of the bottles had a concentration equivalent to 5 milligrams of iron per cc., while that in the other two was twice as strong. The contents of one of each pair of bottles was analyzed at intervals, as stated below, while the remaining bottle of each pair was undisturbed until after the last analysis of the contents of its mate had been made.

Percentage Decline in Concentration.

		Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.
Dec. 24, 1892	1.1		0.68	
May 31, 1893	14.5		8.92	
Oct. 4, 1893	29.8		20.10	
March 16, 1894	42.4	10.8	30.70	8.1

It will be noticed that in both cases the loss of strength was smaller in those bottles which were undisturbed until the expiration of the period of observation. The explanation of this is probably to be found in the fact that the interior of the bottles on the side toward the sun was covered with a film of oxide, which, in the case of the undisturbed bottles, remained intact, while in those from which portions were withdrawn from time to time for analysis, the film was to a great extent detached from the glass. In other words, it is supposed that the solutions were protected in varying degrees by this film from the influence of the direct rays of the sun.

The preceding experiments (1–7) were made with solutions from which the oxide had been carefully excluded, while in those which follow (8–12) weighed quantities of the oxide were added to the solutions of permanganate. As already explained, it was necessary to dry the oxide at a low temperature in order to obtain it in a weighable condition; and, since a precipitated oxide so dried loses some oxygen which is recovered in contact with permanganate, a small portion of the observed loss in concentration is to be ascribed to the reoxidation of the suspended oxide.

8. *June 14, 1892.*—Added to 250 cc. of permanganate solution which had been filtered through glass wool 0.5 gram of manganese oxide. The concentration of the solution was equivalent to 5.278 milligrams of iron per cc. The bottle was kept in mildly diffused light until Oct. 14, 1892, and then analyzed. The loss in strength amounted to 34.62 per cent. This experiment is to be compared with Nos. 1 and 2.

9. Dates, volume of solution, quantity of oxide, and relation to light the same as in No. 8, but the concentration of the solution was equivalent to 14.379 milligrams of iron per cc. The loss of strength was 78.86 per cent. This experi-

ment is to be compared with Nos. 3 and 4, in which solutions of the same concentration, but without oxide, were placed in darkness and diffused light.

It should, perhaps, be explained that the summer of 1892, during which experiments 1, 2, 3, 4, 8, and 9 were made, was one of unusually high temperature in this locality, and that the observed quantitative effects are therefore not strictly comparable with those recorded in connection with other experiments.

10. *Dec. 10, 1892.*—Placed in darkness four bottles, each containing one liter of permanganate solution which had been filtered through asbestos, and to each of which had been added 0.5 gram of oxide. The solution in two of the bottles had a concentration equivalent to 5 milligrams of iron per cc., while that in the other two was twice as strong. The solution in one of each pair of bottles was analyzed on the dates given below, but the remaining bottles were not disturbed until the date of the last analysis.

Percentage Decline in Concentration.

	Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.	
May 31, 1893	11.5		5.9	
Oct. 4, 1893	13.2		7.0	
Mar. 16, 1894	14.8	11.9	7.6	6.8

It will be seen that the absolute reduction in the solutions of different concentration was approximately the same, though the solutions which were unopened, lost less of their active oxygen than those from which liquid was withdrawn from time to time. The relatively large reduction which occurred prior to May 31, may be explained, in part at least, by the loss suffered in restoring oxygen to the oxide.

11. Dates, solutions, and quantities of oxide the same as in the preceding experiment. The bottles, however, were placed in diffused light.

Percentage Decline in Concentration.

	Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.	
May 31, 1893	11.3		6.1	
Oct. 4, 1893	13.0		6.9	
March 16, 1894	14.9	12.1	7.6	7.0

Experiments 10 and 11, are comparable with Nos. 5 and 6. On comparing the first two with each other, it appears that it makes little difference as regards stability whether a solution of permanganate is kept in darkness or in diffused light.

12. Dates, solutions, and quantities of oxide the same as in Nos. 10 and 11, but the bottles were placed in a window facing to the south.

Percentage Decline in Concentration.

	Equiv. 5 mgs. Fe.		Equiv. 10 mgs. Fe.	
May 31, 1893	29.4		16.9	
Oct. 4, 1893	50.6		30.2	
March 16, 1894	67.4	22.9	41.5	14.7

Here, as in No. 7, a great difference is to be observed between the reduction accomplished in bottles from which liquid was withdrawn from time to time, and in those which were undisturbed until the date of the last analysis. The only obvious cause of this difference has been referred to in connection with experiment No. 7. If the results of this experiment are compared with those of No. 7, it will be seen that, though a solution of permanganate free from oxide is decomposed by sunlight, this decomposition is accelerated by the addition of oxide.

It appears from the results obtained in experiments 10 and 11, that when a permanganate solution is reduced by suspended oxide in darkness or in diffused light, the amount of the reduction is probably nearly, if not quite, independent of the concentration of the solution. On the other hand, an observation previously referred to, namely, that solutions which have once begun to lose strength decline in concentration with increasing rapidity, made it appear probable that the rate of decomposition stands in some direct relation to the quantity of the oxide. The following experiment (13) bears upon this question.

13. *Feb. 11, 1893.*—Placed in diffused light half-liter portions of permanganate solution (concentration equivalent to 4.96 mgs. Fe per cc.). One of these (No. 1) contained no oxide, while to the others were added quantities of oxide as

follows: No. 2, 0.25 gram; No. 3, 0.5 gram; No. 4, 1 gram; No. 5, 2 grams; No. 6, 4 grams. The solutions were analyzed Oct. 5, 1893, and the losses expressed in percentage of original concentration were found to be as follows:

No. 1 (no oxide)	0.00
No. 2 (0.25 gram oxide)	4.29
No. 3 (0.5 gram oxide)	14.45
No. 4 (1.00 gram oxide)	29.26
No. 5 (2.00 grams oxide)	59.44
No. 6 (4.00 grams oxide)	entirely decomposed

Except in the case of No. 2, the reduction is nearly proportional to the quantity of oxide.

Another series of bottles containing a solution of equal concentration and volume and the same quantities of oxide respectively, were placed in sunlight and analyzed on the same dates. The losses observed were:

No. 1 (no oxide)	26.64 per cent.
No. 2 (0.25 gram oxide)	30.95 " "
No. 3 (0.50 gram oxide)	31.80 " "
No. 4 (1.00 gram oxide)	39.75 " "
No. 5 (2.00 grams oxide)	61.34 " "
No. 6 (4.00 grams oxide)	entirely decomposed

We have frequently had occasion, in the course of this and other work closely related to it, to determine the ratio of active oxygen to manganese in the oxide resulting from the decomposition of potassium permanganate in solution; and we have invariably found that the ratio, so long as any unreduced permanganate remained, is 1 : 1, just as it is when an oxide is prepared by adding manganous sulphate to an excess of potassium permanganate, both solutions being hot and the latter having been acidified with nitric acid. The following record of analytical results is given in confirmation of the statement:

	Calculated ratio for MnO_2.	Ratio found.
No. 1	1 : 1	1 : 0.999
No. 2	"	1 : 1.000
No. 3	"	1 : 1.000
No. 4	"	1 : 0.999
No. 5	"	1 : 1.001
No. 6	"	1 : 0.999

On the other hand, analyses of the precipitated oxide, made at varying periods after the disappearance of the permanganate color, have indicated a smaller proportion of active oxygen. Considering the precipitates in question as consisting of manganese and oxygen only, the ratios found would give formulas ranging between MnO 90 MnO_2 and MnO 40 MnO_2.

The liquid which remains after the complete reduction of potassium permanganate in solution has a neutral reaction, indicating that all of the potassium of the permanganate is in combination with the oxide. The liquid is yellow in color, has a very slight oxidizing power, and when it is evaporated, a minute residue is obtained which, on heating and moistening with water, gives an alkaline reaction. These properties of the liquid—the color, etc.—are, however, believed to be due to the suspended oxide rather than to substances in solution which differ in composition from the precipitate, since by repeated filtration through asbestos, a colorless liquid may be obtained which has no oxidizing power, and which leaves no appreciable residue on evaporation. These facts have an important bearing on a method recently published in this journal[1] for the mutual standardization of potassium permanganate and sulphuric acid, for they are believed to show that the presence of free alkali in a carefully filtered solution of the commercial salt is not to be feared.

II.

When Permanganic Acid is Reduced by Precipitated Superoxide of Manganese, Three-fifths of the Active Oxygen in the Former Compound is Evolved in the Free State.

In other words, the reduction is in accordance with the equation:

$$2HMnO_4 + XMnO_2 = H_2O + (X + 2)\,MnO_2 + 3O.$$

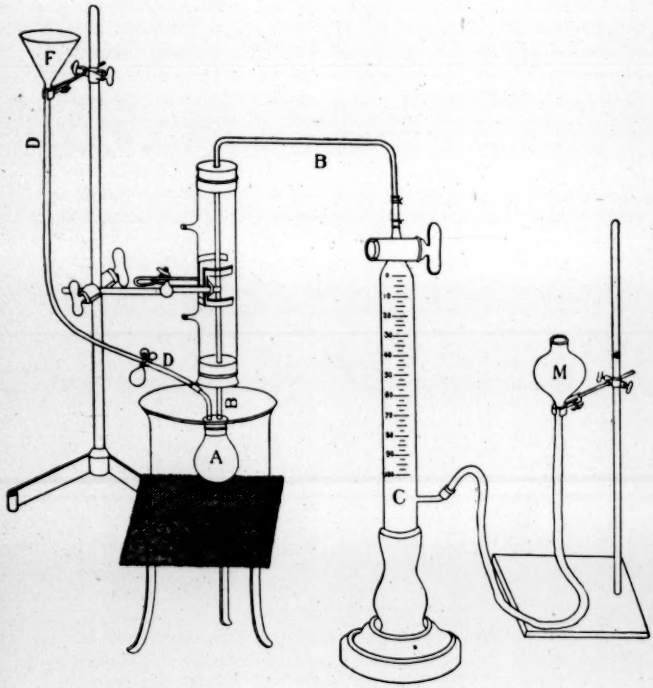
Some evidence of the correctness of this interpretation of the reduction has already been given under I, *e*. In the experiments which follow, the attempt is made to test the quantitative aspects of the reaction by means of a measurement of the oxygen liberated.

[1] Vol. 18, 236.

The apparatus which was used is represented in the accompanying figure. It consisted of

(1) A flask, A, of about 50 cc. capacity, which was closed with a doubly perforated rubber stopper. Through one hole of the stopper passed

(2) A small glass tube, BB, running about 40 cm. above



the flask and then bending to two right angles. The longer limb was surrounded by a condenser, while the shorter one was connected with

(3) A Schiff's azotometer, C, filled with mercury. In use it was found better to have a small quantity of water above the mercury column.

(4) Through the second hole of the rubber stopper passed a short piece of glass-tubing, bent obliquely to clear the lower end of the condenser. This was connected with the funnel, F, by means of the rubber tube, DD.

The method of work was as follows :

The reservoir M was raised to fill C and the stop-cock closed. F and DD were filled with water, and the latter closed at a point near the flask by a pinch-cock, after which F was lowered to give a descending curve to the rubber tube.

A, containing the material to be experimented upon, was placed in position and the stop-cock of the azotometer opened.

After heating the flask in a water-bath kept at the boiling point until it was desired to ascertain how much oxygen had been evolved, water was allowed to run into it through F and DD, and to force all of the gas in A and BB, into the azotometer.

The volume of the gas having been measured, the oxygen in it was determined by absorption in a Hempel pipette, filled either with phosphorus or with an alkaline solution of pyrogallol.

Finally, in order to ascertain what proportion of this oxygen belonged with the residual nitrogen as a constituent of the air in A and BB at the beginning of the experiment, a determination of the oxygen in the atmosphere of the laboratory was made with the same azotometer.

Since the reduction of potassium permanganate by the superoxide in a neutral solution is too slow for convenient observation, all the solutions in the experiments recorded below were mildly acidified with tenth-normal nitric acid. In each case, however, the quantity of acid which was added bore some definite numerical-molecular ratio to the permanganate in solution.

In every experiment, three sets of apparatus like that described, were employed, all the flasks of which were immersed in the same water-bath, in order to secure like conditions of temperature.

No. I contained a weighed quantity of the superoxide and a measured volume of tenth-normal nitric acid.

No. II contained measured volumes of a standard solution of potassium permanganate and of tenth-normal nitric acid.

No. III contained measured volumes of the same permanganate and nitric acid as No. II, and, in addition, the same weight of oxide as No. I.

The contents of all the flasks were diluted with water to the same volume.

The quantities of acid were, in general, so regulated as to produce the same degree of acidity in the three flasks, supposing one molecule of nitric acid to be neutralized by the potassium of a molecule of permanganate. This rule was rigidly adhered to with respect to Nos. I and III, but sometimes departed from in the case of No. II.

The object of thus associating Nos. I and II with No. III was to ascertain whether, under the given conditions, either the superoxide or the free manganic acid separately can yield an appreciable quantity of free oxygen. It was thought that the evolution of a larger volume in No. III must be interpreted as the direct effect of the reducing action of the superoxide upon the permanganic acid.

We give by way of illustration a brief account of the first experiment; but, since the subsequent ones did not differ from this in any essential particular, we present the conditions and results of later experiments in tabular form:

Flask No. I.

Weight of superoxide, 150 mgs.

Tenth-normal nitric acid, 14.28 cc. (equivalent to Mn in $KMnO_4$ in No. II or No. III).

Water, 27.12 cc. (total volume of solution, 41.40 cc.).

Flask No. II.

Potassium permanganate solution, 20 cc. containing 112.48 mgs. $KMnO_4$.

Tenth-normal nitric acid, 7.14 cc. (equivalent to K in $KMnO_4$).

Water, 14.26 cc. (total volume of solution, 41.40 cc.).

Flask No. III.

Potassium permanganate, 20 cc. containing 112.48 mgs. $KMnO_4$.

Tenth-normal nitric acid, 21.40 cc. (equivalent to K + Mn in $KMnO_4$).

Weight of superoxide, 150 mgs.

The nitric acid remaining free in No. III after the neutralization of the potassium in the permanganate was equal to that free in No. I, while No. II may be supposed to contain only free permanganic acid.

The three flasks were immersed to the same depth in the bath and the water in the latter was kept boiling for three hours. During this time a diminished pressure equal to about 50 mm. of mercury was maintained as nearly as possible by lowering from time to time the reservoirs connected with the azotometers.

No evolution of gas could be observed, either in No. I or in No. II. In No. III, on the other hand, a visible evolution of gas began as soon as the flask was lowered into the hot water, and within five minutes the deep purple color of the permanganate had given place to a delicate pink which persisted for about ten minutes, when it also disappeared. Immediately after the disappearance of the color, the liquid was seen to be filled with a brown oxide which remained suspended for about thirty-five minutes, when it subsided, leaving a perfectly clear supernatant solution. During this subsidence of the oxide a slight increase in the volume of gas in the azotometer was noticed, but after fifty minutes the volume of the gas appeared to remain stationary.

Results.

		I. cc.	II. cc.	III. cc.
Total air and oxygen,	=	42.60	52.40	60.60
Nitrogen after absorption of oxygen,	=	34.00	40.90	37.80
Oxygen,	=	8.60	11.50	22.80
Air = 79.8 per cent. nitrogen, 20.2 per cent. oxygen, Oxygen of air = nitrogen found $\times \frac{20.2}{79.8}$	=	8.60	10.353	9.57
Oxygen obtained,	=	0.0	1.147	13.23

Temperature = 21° C.
Barometer = 737 mm.
Oxygen obtained at normal, = 0 1.033 11.913
The 20 cc. $KMnO_4$ = 112.48 mg
1 atom of oxygen = 7.967 cc.
Atoms oxygen found from one molecule $KMnO_4$, = 0 0.129 1.496

In the table which follows are presented the results of a series of twenty-three determinations made exactly as described in the foregoing example. The first column under each of the three designations—Flask I, Flast II, and Flask III,—gives the quantity of liberated oxygen expressed as atoms per molecule of the permanganic acid in No. II or No. III, while the second column under the same headings gives the number of molecules of nitric acid per molecule of the same permanganic acid.

Three-hour Determinations.

	Flask I.		Flask II.		Flask III.	
	MnO_2 (150 mg.)	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.
1	0.00	2	0.13	1	1.495	3
2	0.00	2	?	1	1.493	3
3		2	0.13	3	1.532	3
4	0.00	2	0.21	3	1.466	3
5	0.03	2	0.10	3	1.467	3
6	0.02	2	0.25	3		3
7	0.06	2	0.08	3	1.526	3
8	0.04	2	0.15	3	1.527	3
9	0.04	2	0.11	3	1.504	3
10		2	0.20	3	1.504	3
11	0.03	2	0.14	3	1.516	3
12	0.00	2	0.18	3	1.524	3
13	0.03	2	0.25	3	1.559	3
14	0.05	2	0.26	3	1.574	
15	0.02	1	0.32	2	1.552	2
16	0.03	1	0.31	2	1.583(?)	2
17	0.04	1	0.31	2	1.512	2
18	0.01	1	0.32	2	1.466	2
19	0.00	1	0.18	2	1.412	2
20	0.01	1	0.36	2	1.411	2
21	0.06	1	0.22	2	1.402	2
22	0.00	1	0.30	2	1.495	2
23		2	0.08	3	1.469	3
				Average	1.4995	

The small quantities of oxygen obtained in flask No. II indicate that permanganic acid is somewhat unstable under the conditions of the work, but it does not appear that its instability is materially increased by the presence of a moderate amount of free nitric acid.

The oxygen obtained in flask No. III, ranges from 1.402 (Exp. 21) to 1.574 (Exp. 14) with an average of 1.4995 atoms per molecule of permanganic acid. These numbers approximate sufficiently to the value 1.5 (three-fifths of the active oxygen of $HMnO_4$), to show that the reduction is probably in accordance with the equation previously given.

There are, however, two sources of error in all of these experiments, but, since they tend in opposite directions, the results are vitiated only by their difference. In the first place, the oxide which was used in the reduction, contained less oxygen, as has already been explained, than is normal to the superoxide, and the lacking oxygen is recovered in the presence of permanganic acid. The effect of this reaction is, of course, to diminish the quantity of oxygen liberated. On the other hand, the oxide itself loses some oxygen when, as in all the cases covered by the table, the period of heating is extended beyond the time of the disappearance of the color of the permanganic acid, and thus some of the oxygen lost in the first instance is regained. How perfectly the two sources of error balance each other could be ascertained only by determining the oxygen, both in the oxide employed for the reduction and in the oxide resulting from the reduction. But, as will be seen, we have ascertained in another way that our results are not greatly vitiated by the causes in question.

In this connection, it seemed to us important to establish the fact that the oxide does lose oxygen when, as in the experiments recorded, the heating is continued beyond the time of the disappearance of the color. It has already been stated that the color of the permanganate disappeared within fifteen minutes, leaving the oxide in a state of suspension, and that within the next thirty-five minutes the oxide subsided, leaving the supernatant liquid clear. Since during this subsidence of the oxide an increase in the volume of the gas was observed, it was interpreted as an evidence of the reduction

of the oxide. We therefore made a series of experiments in every respect like the preceding ones, except that the liberated oxygen was determined after heating for fifteen minutes in the bath. The results are given below:

Fifteen Minute Determinations.

	Flask I.		Flask II.		Flask III.	
	MnO_2 (150 mg.)	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.
1	0.05	1	0.08	2	1.340	2
2	0.04	1	0.05	2	1.325	2
3	0.06	1	0.05	2	1.335	2
4	0.00	1	0.00	2	1.347	2
5	0.03	1	0.03	2	1.412	2
6	0.02	2	0.02	3	1.363	3
7	0.02	2	0.06	3	1.377	3
8	0.00	2	0.02	3	1.363	3
				Average	1.358	

The difference between 1.358 (the average number of atoms of oxygen per molecule of permanganic acid, which was obtained in the above series of experiments) and 1.5 (three-fifths the number of atoms of active oxygen in a molecule of permanganic acid), is believed fairly to represent the loss of the permanganic acid in restoring to the oxide the oxygen it had lost in drying.

Still another series of determinations were made in order to ascertain whether all the oxygen conveyed to the oxide by the permanganic acid is liberated during the subsidence of the oxide which follows the disappearance of color. Since the liquid lost color and became clear within fifty minutes, the period of heating was limited to that time:

Fifty Minute Determinations.

	Flask I.		Flask II.		Flask III.	
	MnO_2 (150 mg.)	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.	$KMnO_4$ 20 cc. = 112.48 mg.	$\frac{N}{10}$ HNO_3 No. of molecules.
1	0.04	1	0.06	2	1.564	2
2	0.04	1	0.11	2	1.491	2
3	0.05	1	?	2	1.512	2
4	0.03	1	0.05	2	1.532	2
				Average	1.525	

It appears from the above results that all of the oxygen which was lost by the permanganic acid in the higher oxidation of the oxide used for the reduction is again liberated during the subsidence of the oxide after the disappearance of the color. In other words, the two sources of error which were mentioned as affecting our work were of nearly equal magnitude, and therefore neutralized each other quite exactly.

Summary.

1. Permanganic acid and potassium permanganate are reduced by precipitated superoxide of manganese with liberation of three-fifths of the active oxygen of the permanganic acid.

2. To this cause is to be ascribed the observed instability of standard solutions of potassium permanganate. Such solutions should, therefore, be carefully filtered through asbestos and thereafter protected.

3. Solutions of potassium permanganate which are free from suspended oxide exhibit a high degree of stability whether kept in darkness or in diffused light. Even pure solutions are, however, decomposed in direct sunlight.

4. The oxide resulting from the complete reduction of a neutral solution of potassium permanganate contains all of the potassium of the original salt, and the supernatant liquid is, therefore, neutral.

5. Whether the precipitated superoxide is formed by the slow decomposition of a neutral solution of potassium permanganate or by the addition of manganese sulphate to an acidified solution of permanganic acid, the ratio of oxygen to manganese in it remains normal (*i. e.*, 2 : 1) only so long as there is present unreduced permanganate or permanganic acid. In the absence of permanganic acid or its salt, the oxide loses oxygen even at ordinary temperatures.

6. In the presence of permanganate or permanganic acid, the lost oxygen is restored.

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REVIEWS AND REPORTS.

A REVIEW OF SOME IMPROVEMENTS IN CHEMICAL INDUSTRY.

In the earlier numbers of this JOURNAL there appeared a series of papers on the technical applications of chemistry, by Prof. J. W. Mallet. Ten years later, in 1889, Prof. S. B. Newbury contributed several articles upon the advances made in this direction during the interval.

In these pages the writer will endeavor to show a few of the notable improvements introduced during the past five or six years, with an occasional reference to some of the failures, and to the more promising inventions which may be developed in the future.

Heavy Chemical Manufactures.

Sulphur.—Sicily continues to furnish the larger part of the world's supply of sulphur, although many of the mines are now idle. The industry has suffered a period of great depression since 1890, and the price in 1895 had fallen to about $16 per ton for seconds and $15 for thirds. A few operators have attempted to introduce more modern appliances for mining, the better to meet low prices, but in most cases this has only been done after a struggle against native prejudice, even resulting in riots at the mines.

In the methods of extracting sulphur from the gangue little advance has been made since the papers of Professors Mallet[1] and Newbury[2] were published. The "calcerone" is most generally employed, though melting out the sulphur by the use of solutions of calcium chloride[3] is used to some extent. Extraction by means of carbon disulphide has made little progress.

Japanese sulphur has become a considerable competitor with the Sicilian, and in these mines are found many modern improvements and economical working. Late statistics show that 84 mines were in operation in 1894. A new sulphur deposit of probable future importance is being developed on the island of Tanna, New Hebrides. A rich ore, with cheap labor and fuel at hand may make this even a more formidable rival of Sicily.

Our domestic production has fallen until it scarcely deserves notice, but little more than 400 tons being produced in 1894. An innovation recently introduced in the Nevada mines, is a plant for hydraulic mining to remove the overlaying surface earth. The method of extraction employed in

[1] J. W. Mallet: This JOURNAL, 1, 273. [2] S. B. Newbury: *Ibid*, 11, 124.
[3] Vincent: Bull. Soc. Chim., 40, 528.

this country is the Dubois[1] process of distillation with steam in rotary retorts. The deposits of Louisiana and Texas have not been developed.

Of the several recovery processes for sulphur from the tank waste of the Leblanc soda industry, only the Chance-Klaus[2] method has proved practical on a large scale. This can be so managed that a large part of the product is obtained as "flowers of sulphur," which finds a ready sale because of its purity and attractive appearance. But the process has not apparently met the original expectations of its promoters, for in 1894 England imported 20,100 tons of sulphur besides their imports of pyrites. Apparently about 12,000 or 15,000 tons are now recovered annually, though exact figures have not been obtainable. In 1893 the United States imported about 10,000 tons of sulphur from Great Britain, of which a considerable part was probably recovered sulphur.

The manufacture of wood-pulp by the sulphite process has stimulated the demand for sulphur within the past few years in this country.

Pyrites.—The use of pyrites for sulphuric acid is constantly increasing, but owing to the very low price of brimstone for the past two years, a few acid makers who had not destroyed their old brimstone burners, returned to the use of sulphur. Mr. K. F. Stahl[3] presented the relative merits of brimstone and pyrites, in a paper published about three years ago, and figured a difference of three cents per ton of 50°Bé acid, in favor of brimstone; but he based his estimate on pyrites at $6 per long ton. E. W. Parker[4] shows, however, that the actual cost of pyrites in 1893, was less than $3.50 per long ton and pyrites acid of 50°Bé really cost $5 per ton, against $6.25 for brimstone acid. Since our native pyrites are nearly free from arsenic and contain but little copper, there appears to be no good reason for the continued use of brimstone, except for a special acid free from all traces of arsenic, copper or zinc. Even at the present price of brimstone, the other items remaining the same, a decided advantage remains with the pyrites acid.

Improvements in the business have resulted in the production from pyrites of an iron oxide containing only 1 to 2 per cent. of sulphur. This now finds a somewhat restricted use in the arts and as an iron ore. Residues from Spanish pyrites containing copper are of course valuable ores for that metal.

Sulphuric Acid.—The chief advances in sulphuric acid making have been in the improvement of details rather

[1] J. Soc. Chem. Ind., *1887*, 439, 442; *1889*, 696. [2] J. Soc. Chem.. Ind., *1888*, 163
[3] J. Anal. Appl. Chem., *1892*, 690. [4] Mineral Resources of U. S., *1893*, 745.

than in radical changes of apparatus or system. Mechanical furnaces have been introduced in some works recently, and generally give good results. They seem to be particularly good for burning "fines," since they allow no excessive introduction of air during raking. Muffle furnaces of the Spence type of mechanical burners have proved successful for roasting zinc blende, the muffle being heated by generator gas. The waste heat of the fire is utilized to heat the air by which the blende is oxidized. The ore is charged through a hopper into the top shelf of the burner and raked down by mechanical rakes from one shelf to the next. Some recent kilns of this kind will roast about 42 tons of ore carrying 28½ per cent. sulphur, in twenty-four hours, not more than 1 per cent. sulphur being left in the roasted ore. For making sulphuric acid, the gases from blende-roasting are treated in much the same way a those from pyrites. Since the amount of sulphur in blende is not sufficient to support the combustion, the roasting is accomplished by the aid of external application of heat to the muffles.

The Lunge-Rohrmann perforated plates are generally considered unsuitable for use in the Glover tower (though the inventors did not recommend them for this purpose),[1] because the high temperature would cause them to crack and impure gases might clog the openings. But placed in towers between the chambers they undoubtedly are effective. Their great cost, together with the fact that they offer considerable resistance to the movement of the gases, hinder their more general use. The "pipe columns" of Gilchrist[2] and Hacker have been introduced in several acid works in this country but in one case, at least, proved a failure. In other cases, however, under different conditions they seem to give very satisfactory results. Their chief advantage appears to be a more thorough mixing of the gases as they pass from one chamber to the next. The cause of the one failure above mentioned is attributed to improper placing of the towers, on the theory that their chief function is to *cool* the gases.

In some acid works, instead of steam jets in the outlet pipes, fans are used to assist in the movement of the gases, and give better results.

The more modern form of Glover tower has a steel frame and is lined with acid-resisting brick on tile. Quartz is still in favor as packing for these towers.

The general trend of improvement appears to be in the direction of smaller chambers and increased tower capacity. One of the latest ideas of this kind is embodied in Barbier's

[1] J. Soc. Chem. Ind., *1893*, 232. [2] J. Soc. Chem. Ind., *1894*, 1142.

Tower System,[1] in which the lead chambers are entirely abolished and a system of towers substituted for making the acid. The scheme has hardly advanced beyond the experimental stage as yet, but gives promise of future importance. In this system the gases from sulphur or pyrites burners are led into a series of towers, five or six in number, connected by flues from the top of one tower to the bottom of the one adjacent. Beneath each tower is a pan for collecting the acid formed. These pans are set *en cascade*, so that the overflow is by gravity from one to the next, and all are set over a flue leading from a fire grate at the lower end of the series; or they may be heated by the sulphur dioxide gas on its way from the burners to the towers. The towers are filled with perforated pottery vessels of acid-resisting material, thus affording a large surface exposure. A sprinkler at the top of each tower supplies the dilute nitric acid needed. The last tower of the series is a Gay Lussac for absorbing the nitrogen oxides. As it is formed, the acid collects in the pans beneath the towers and flows from one to the next, always approaching the fire and becoming more concentrated in each pan, the denitration being accomplished at the same time. The water vapor and nitrogen gases pass off from the pans and immediately back into the towers. The final concentrating pan is set directly over the fire and not under any tower, and in it the acid reaches a gravity of about 60° Bé.

The advantages claimed for this system are, a more concentrated pan acid, free from nitrogen; larger yield per cubic meter of tower space compared with the cubic capacity of chambers; adaptability to use in both warm and cold climates, the temperature in the tower being high, (about 90°C); the cost of construction not exceeding one-half that for a chamber plant of the same daily output; and a much smaller ground area to be occupied.

While this particular apparatus may not prove entirely successful,[2] there seems no doubt that the tower system is in many ways superior to the chamber process and will probably be much developed in the near future.

Among improvements in the methods of concentration of the acid is to be noted that much of this is now done in the Glover tower, which is so constructed and managed that acid of 62° to 66° Bé may be obtained directly. In some cases two towers are in series, the one next the chambers being the denitrating tower and part of the acid from it is sent through the tower next the burners, by which the acid is concentrated

[1] P. de Boissieu: Bull. Soc. Chim., 11, 726. U. S. Patent No. 535882, March 19, 1895.

[2] Unsatisfactory results with this apparatus are reported from Italy. J. Soc. Chem. Ind., 1895, 698.

up to 64° or 66° Bé, the steam passing along with the sulphur gases into the denitrating tower.

Kessler's[1] apparatus, in more or less modified form, is also being introduced for the concentration of acid. This is a continuous surface heating system used in connection with platinum or iron stills which are fired with generator gas or oil, and the waste fire gases passed over the surface of the acid contained in lead-lined iron tanks.

Cast iron stills are replacing platinum to a great extent, the acid being concentrated to about 64° Bé in the Glover tower and finished in the iron still. The results are very satisfactory and the life of a still is from two to six months.

Gold-lined platinum stills are used to some extent, but their great cost acts as a bar to a more extended application.

Another new idea is the abolition of the "acid-egg," a system of air-lifts similar to those used for raising water from artesian wells, being substituted.

Hydrochloric Acid.—This acid has been the main support of the Leblanc soda process for some years, because of its use in generating the chlorine necessary for making bleaching powder. But few improvements in the manufacture or condensation of hydrochloric acid as derived from the salt-cake process, have been made within recent years. The Lunge-Rohrman plate tower is found quite effective in condensing the acid but when the draught is strong it seems necessary to supplement it with a small coke tower.[2]

Recovery of hydrochloric acid from the waste calcium chloride liquors of the ammonia-soda process has apparently not proved successful on a commercial scale, as yet.

Methods depending upon the decomposition of magnesium chloride by water vapor, have been proposed for use in connection with a modified ammonia-soda process, and also to be applied to the magnesium chloride residues, obtained in the Stassfurt salt works; but though they have been given experimental trials, none of these processes appear to have met with commercial success. Most investigators have attempted only the direct production of chlorine from these residues, and some of these processes will be considered in a subsequent paper.

Nitric Acid.—The old form of iron retort with exposed ends is being replaced by the newer apparatus of Guttman.[3] In this the entire retort is surrounded by flame and furnace gases, thus ensuring nearly equal temperature in all parts, the retort

[1] J. Soc Chem. Ind., *1892*, 434, and *1895*, 156.

[2] Lasche: Ztschr. angew. Chem., *1894*, *1895*, 610; 374.

[3] J. Soc. Chem. Ind., *1892*, 349; *1893*, 203; Ztschr. angew. Chem., *1893*, 37.

being heated to such a high degree that the acid has very little action on the iron. Two of these retorts are usually joined to one condensing apparatus of Guttman's design.

This condenser has found much favor with acid makers and is generally used in more advanced plants. It consists of a series of some twenty vertical pipes of thin-walled earthenware, joined in pairs at the top by elbows and opening at the bottom into a horizontal collecting pipe; this is divided by diaphragms into a series of chambers connected by U tubes passing beneath the diaphragms. The condensing pipes are about two and one-half meters high, twelve cm. diameter, and eight mm. thickness of wall. Air cooling is used in this apparatus. Because of the diaphragms in the horizontal pipe, the acid vapors must pass up one vertical tube and down the next, in order to pass through the system. The condensed acid accumulates in the chambers and passes into a suitable collecting vessel. To absorb the nitrous gases, the uncondensed vapors pass into a Lunge-Rohrmann plate tower through which water or sulphuric acid of 150° Twaddell is trickling.

The condenser is provided with a hot-air injector by which the uncondensed nitrous acid is brought in contact with moisture and air at 76° C, and is converted into nitric acid. The injector also improves the draught through the apparatus, hastening the distillation and removal of the gases from the retort. So little nitrogen peroxide is formed in this apparatus, that the acid needs but very little or no "bleaching" for market, and its strength may reach 40° Bé. About 95 per cent. of the vapors condense in the pipes and 5 per cent. in the Lunge tower. A modification of the apparatus consists of five or six pipes, cooled by a water jacket. In these about 98 per cent. of the vapor condenses. The liquid condensed contains about 96 per cent. of nitric acid and 1 per cent. of nitrogen peroxide. The apparatus is gradually replacing the old system with "bombons" for condensation.

Hart's tube condenser[1] has been introduced in some works and appears to be giving good results. The apparatus is constructed of glass and earthenware tubes, placed above the brick arch over the retort, thus occupying very little floor space. It is simple, easily repaired and needs so little attention that one man can attend to several retorts. The system is based on the theory that nitrogen peroxide, which colors the acid and causes loss to the manufacturer, is produced by too prolonged heating of the acid vapors, and the more rapidly the vapors pass from the retort and are condensed, the

[1] J. Soc. Chem. Ind., *1894*, 1197; J. Am. Chem. Soc., *1895*, 576.

lighter colored will the product be. Among other advantages claimed for the system, is an increased yield of light-colored, concentrated acid with small consumption of condensing water.

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OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN. Engelmann: Leipzig.

No. 68. DAS NATÜRLICHE SYSTEM DER CHEMISCHEN ELEMENTE. L. Meyer and D. Mendelejew. 2.40 marks.

No. 69. UEBER FARADAY'S KRAFTLINIEN. J. C. Maxwell. 2.00 marks.

No. 70. MAGNETISCHE POLARISATION DER METALLE UND ERZE DURCH TEMPERATUR-DIFFERENZ. T. J. Seebeck. 2.00 marks.

No. 72. CHEMISCHE ANALYSE DURCH SPECTRALBEOBACHTUNGEN. G. Kirchhoff and R. Bunsen. 1.40 marks.

No. 74. UNTERSUCHUNGEN UEBER DIE GESETZE DER VERWANDSCHAFT. C. L. Berthollet. 1.80 marks.

Among the recent issues of Ostwald's neat and inexpensive reprints of classical papers are the very important ones cited above. The four famous papers by Lothar Meyer (1864–1869) and Mendelejew (1869–1871) are edited and annotated by Karl Seubert; Maxwell's first paper (1856) on Faraday, from the Cambridge Transactions, is translated and discussed by Boltzmann in a truly magnificent manner; the early work on the electrochemistry of thermocurrents, Seebeck (1823), is edited by von Oettingen; and the remaining volumes are issued by Ostwald. The first of them comprises the two papers by Kirchhoff and Bunsen (1860), announcing the discovery of spectrum analysis and its first great results, among which the discovery of caesium and rubidium are prominent; while the other is a translation of the brilliant and very inaccessible original paper of Berthollet (1801) on chemical affinity. The annotations and biographical notes are in every case of the greatest interest. J. E. T.

REVIEW OF AMERICAN CHEMICAL RESEARCH. ARTHUR A. NOYES, Editor.

Attention is here called to an important literary undertaking of interest to chemists. Dr. Noyes, of the Massachusetts Institute of Technology, conceived the idea of bringing together abstracts of all articles embodying the results of original work done in America in the field of chemistry, and publishing them regularly in the *Technology Quarterly*. In a preliminary note the Editor says: "The purpose of this publication, which is hereafter to appear serially in this JOURNAL, is to present in a concise form a review as complete as possible of all original work having a chemical bearing, published in the United States after the beginning of the year 1895. It is believed that such a compilation will prove of

more than usual value in the case of the research work of this country, by reason of the fact that so large a proportion of it is published in other than chemical journals, and thus fails to become incorporated with the rest of the science, and also because the abstracts of American chemical literature published in foreign journals are very incomplete."

The execution of the plan has been made possible by the coöperation of members of the instructing staff of the Institute of Technology.

Three instalments of the Review have been issued and an examination shows that the work thus far has been carefully done. I. R.

ORGANIC CHEMISTRY. THE FATTY COMPOUNDS. By R. LLOYD WHITELEY, F. I. C., F. C. S., Principal of the Municipal Science School, West Brunswick; Late Lecturer and Demonstrator in Chemistry in University College, Nottingham. London: Longmans, Green & Co. and New York: 1895. 291 pp.

This book calls for very little comment. It is clearly written and may prove useful to some students, but there are better books available about as advanced as this. The fatty compounds are here treated in 290 pages. Nothing is said in the Preface indicating that the aromatic compounds are to be treated in a subsequent volume, and the question may fairly be raised—Of what use is a small book on the fatty compounds? Is it possible that there are schools in which a course on these compounds is given and the aromatic compounds neglected? The author's reasoning is not always satisfactory, and does not, therefore, give the student a correct conception of the character of the evidence upon which the prevailing ideas regarding the structure of compounds rest. As an illustration, the reasoning on page 55 in regard to the structure of ethylene may be mentioned. This would not carry conviction to the mind of a thinking student. Some errors have been noted: In the first equation on page 60 the composition of the cuprous compound of acetylene is represented by the formula, $C_2Cu_2H_2O$. This is not correct. Keiser has proved that the compound has the formula C_2Cu_2. On page 7 "Henniger" is given instead of "Henninger." Under Lactic Acid, p. 227, it is stated that the inactive and the dextro-rotatory varieties are known, and no mention is made of the laevo-rotatory acid discovered by Schardinger.

It is, however, hardly fair to emphasize the slight shortcomings of the book. On the whole, it is probably as free from errors as most others and, in many respects, it is worthy of praise.

THE CHEMISTRY OF POTTERY. BY KARL LANGENBECK, Superintendent of the Mosaic Tile Company, Zanesville, O., formerly Superintendent of Rookwood Pottery, Chemist of the American Encaustic Tiling Company, etc. Easton, Pa.: Chemical Publishing Co. 1895. 197 pp. Price, $2.00.

The object of this book is thus stated by the author: "While to many of our chemists, engaged in developing the natural resources of the country, the clays found on every side have seemed to offer a fruitful field for investigation, the information at command concerning the chemical needs of the potter has been so meager, that their efforts have been practically abortive. The thousands of analyses published are mostly worthless, because they do not go far enough or because unaccompanied by essential physical tests and practical trials.

"It is hoped that this little treatise will supply information that will turn future labors in this channel to good account.

"The writer is well aware that in confining the subject matter to the results of his personal experience, the shortcomings of the treatise are numerous and manifest; but he believes as such it is a more direct expression of the practical needs of the working potter, and therefore of more immediate value, than a compilation of the published work of European chemists on their ceramic industries."

The book is made up of fifteen chapters with the following titles: 1. Analysis of Pottery Materials and Products; 2. Physical and Empirical Tests; 3. Pyrometry; 4. Classification of Ceramics; 5. Pottery Glazes; 6. Red Ware; 7. Rockingham and Yellow Ware; 8. Stoneware; 9. Raw Materials of White-Ware Bodies; 10. White Granite and Cream-colored Ware; 11. Majolica and Enameled Tile; 12. White Enameled Brick; 13. Floor Tile and Terra Cotta; 14. Refractory Materials; 15. Burning the Ware.

In view of the extensive experience of the author there can be no doubt of the value of this book.